3.0 Data Analysis

This chapter provides results of the monitoring and analysis of data collected by the Project's monitoring sites from mid-December 2004, as monitoring equipment began, to May 21, 2016, when air-monitoring operations ended. The monitoring sites in the network are shown in Figure 1-1, on page 1-4, and their equipment and instrumentation is described in Table 3-1, below.

Table 3-1. Schedule of air monitoring sites, their equipment and major instrumentation

TCEQ CAMS#	Description of Site Location	Monitoring Equipment				
		Auto GC	**TNMHC(T) Canister(C)**	**H_2S & SO_2**	**Met Station**	**Camera**
634	Oak Park Recreation Center (**OAK**)	Mar 2005 to May 2016	C: Dec 2004 to Feb 2009 T: Dec 2004 to Apr 2012		Dec 2004 to May 2016	
629	Grain Elevator @ Port of Corpus Christi (**CCG**)		T&C: Dec 2004 to May 2016	Dec 2004 to May 2016	Dec 2004 to May 2016	
630	J. I. Hailey Site @ Port of Corpus Christi (**JIH**)		T&C: Dec 2004 to May 2016	Dec 2004 to May 2016	Dec 2004 to May 2016	
635	TCEQ Monitoring Site C199 @ Dona Park (**DPK**)		T&C: Dec 2004 to May 2016	Dec 2004 to date	Dec 2004 to date	Jan 2005 to May 2016
632	Off Up River Road on Flint Hills Resources Easement (**FHR**)		T&C: Dec 2004 to May 2016	Dec 2004 to May 2016	Dec 2004 to May 2016	
633	Solar Estates Park at end of Sunshine Road (**SOE**)	Mar 2005 to date	C: Dec 2004 to Feb 2009 T: Dec 2004 to Apr 2012	Dec 2004 to May 2016	Dec 2004 to date	Jan 2005 to May 2016
631	*Port of Corpus Christi on West End of CC Inner Harbor (**WEH**) (site terminated)*		T&C: Dec 2004 to May 2012	Dec 2004 to May 2012	Dec 2004 to May 2012	

Legend

CAMS	continuous ambient monitoring station
Auto-GC	automated gas chromatograph
TNMHC	total non-methane hydrocarbon analyzer (all except CAMS 633 & 634 also have canister hydrocarbon samplers)
H_2S	hydrogen sulfide analyzer
SO_2	sulfur dioxide analyzer
Met Station	meteorology station consisting of measurement instruments for wind speed, wind direction, ambient air temperature and relative humidity
Camera	surveillance camera

To aid in understanding the analyses in this chapter, a glossary of terms is provided in Section 3.8, pages 3-133 to 3-136, at the end of this chapter.

3.1 Characteristics of the Corpus Christi, Texas Urban Area

The prevailing winds in the Corpus Christi area are from the southeast. Figure 3-1, below, shows a histogram of wind direction measurements combining data from several sites, showing that 50 percent of wind direction measurements fall between 106 degrees (east-southeast) and 174 degrees (south-southeast), and the lowest frequency of winds is from the west (210 – 300 degrees). Table 3-2, page 3-3, shows the mean wind speed in miles per hour (mph) using all observations from December 2004 to May 2016 (May 2012 for West End Inner Harbor CAMS 631) for the Project and TCEQ monitoring sites. Table 3-2 also shows the 90th percentile wind speed, to reflect the range of speeds typically measured. Sites with higher wind speeds are generally those with better overall exposure with fewer nearby wind obstructions. The Solar Estates CAMS 633 and J. I. Hailey CAMS 630 sites appear to have had the best overall exposure and highest wind speeds.

In Corpus Christi the statistical distribution of wind speeds varies by wind direction. Winds blowing in from the Gulf of Mexico from the southeast tend to be stronger, while winds from the west tend to be the weakest. Coincidentally, winds from the southeast are most frequent, while winds from the west are the least frequent. As an example, the mean wind speed by direction from the Solar Estates CAMS 633 site appears in Figure 3-2, on page 3-3. Graphs of the wind speed and direction distributions appear in the text detailing the results for each project monitoring site.

Figure 3-1. Distribution of wind direction measurements combining several sites' data, 2005-2016

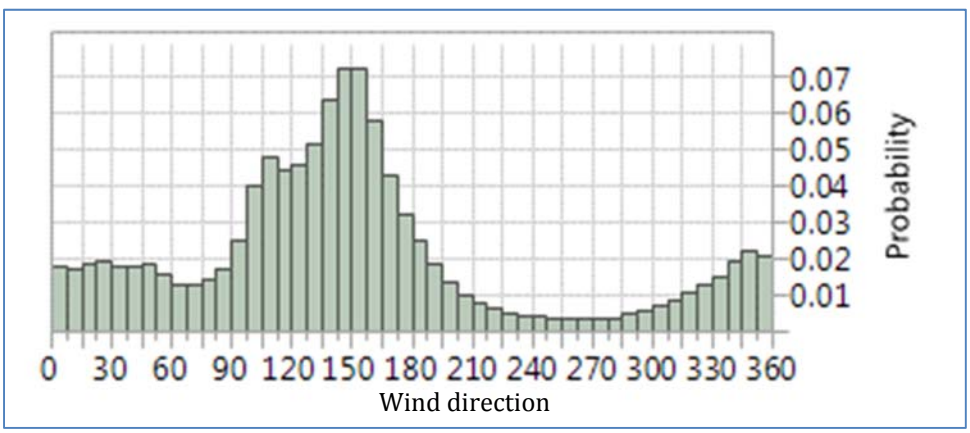
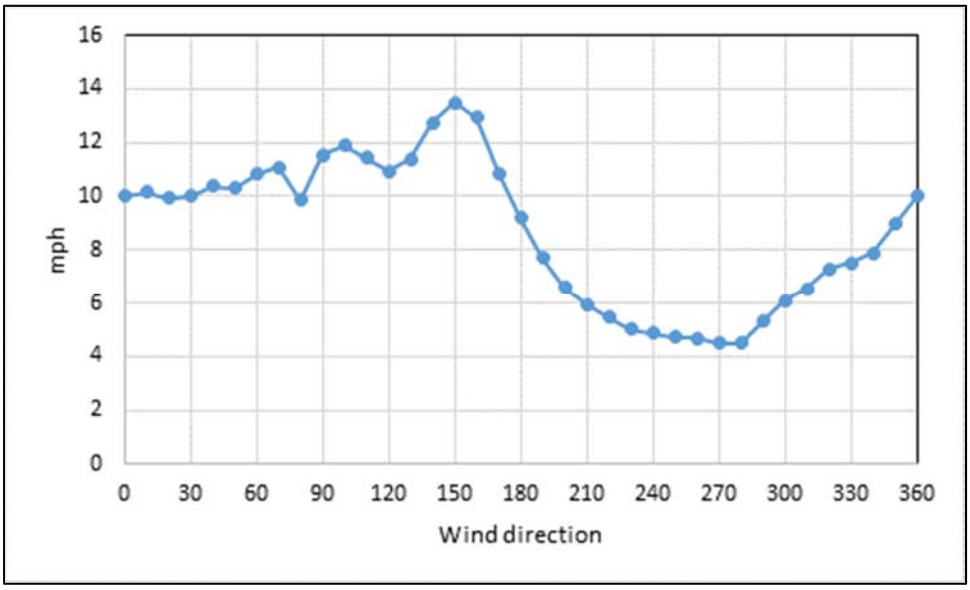


Table 3-2. Wind speed statistics at Corpus Christi sites 2004 – 2016

Site name	Site	Mean wind speed mph	90th p-tile mph
Corpus Christi West	TCEQ C4	9.7	16.4
Corpus Christi Tuloso	TCEQ C21	7.0	11.7
Corpus Christi Huisache	TCEQ C98	9.5	15.1
Port Grain Elevator	UT C629	8.0	12.8
J.I Hailey	UT C630	11.3	17.4
Inner Harbor	UT C631	10.3	16.7
FHR Easement	UT C632	9.2	15.0
Solar Estates	UT C633	10.7	17.9
Oak Park	UT C634	6.8	10.8
Dona Park	TCEQ C635	7.6	12.5
Dona Park	UT C635	7.6	12.6
Williams Park	TCEQ C1024	7.2	11.4

Figure 3-2. Solar Estates CAMS 633 mean wind speed (miles per hour) by wind direction



Several meteorological factors affect the pollutant concentrations measured in this project. In winter months, winds tend to be slower and the air does not mix as much as in the summer, giving air pollutants more opportunities to accumulate. Thus, all else being equal, one can expect higher concentrations for many pollutants in colder weather months. Wind direction also plays an important role because concentrations are generally higher when the wind blows from the direction of an emission source. Wind speeds and directions tend to vary based on the season of the year, with more southerly winds in summer and more northerly winds in winter. In examining all the data taken in this study, the seasonal effects on average concentrations are very evident.

- At the six project sites measuring SO_2, within each individual year, the rank ordering of average concentrations by annual quarter is generally
    - highest in the first quarter (January, February, March),
    - second highest in the fourth quarter (October, November, December),
    - third highest in the second quarter (April, May, June), and

    - lowest in the third quarter (July, August, September).
- At the six out of seven project sites measuring total non-methane hydrocarbons (TNMHC), within each individual year the rank ordering of average concentrations by annual quarter is generally
    - highest in the fourth quarter (October, November, December),
    - second highest in the first quarter (January, February, March),
    - third highest in the third quarter (July, August, September), and
    - lowest in the. second quarter (April, May, June)
- The West End Inner Harbor CAMS 631 site did not show a seasonality pattern for TNMHC.
- For H_2S, the seasonality pattern was not as clear as with TNMHC and SO_2, but there was a general tendency for concentrations to be higher in the second and third quarters.
- For the large majority of hydrocarbons measured by the two Project sites with auto-GCs, the seasonal pattern was highest in average concentrations in either the fourth or first quarter and lowest in either second or third quarter.
- Among hydrocarbons, the exception being the reactive compound isoprene, which is emitted primarily by trees, and at both Project auto-GC sites, average concentrations were highest in the third quarter, followed by the second quarter, followed by the fourth quarter, and then followed by the first quarter.

3.2 Some Notes about the Data used in this Report

The data recorded from instruments at the Project's air monitoring sites come in three broad types categories. 1.) TNMHC, SO_2, and H_2S, and meteorological measurements made continuously, with averages reported every 5-minutes. 2) Auto-GC concentration data from 40-minute duration samples drawn once per hour, and reported as hourly values. 3) Canister data are the result of 20-minute duration samples taken under specific conditions and are aperiodic. Additional information follows:

- TNMHC, SO_2, and H_2S, and meteorological measurements were reported at 5-minute intervals, and 12 five minute values starting from the top of each hour are averaged together to produce a one hour average ($5 \times 12 = 60$ minutes = 1 hour). Each measurement and subsequent one hour value are time-tagged at the start time of the measurement, and recorded in Central Standard Time. Because the pollutant gas instruments are calibrated to work over a large range of pollutant concentrations, it is possible that an actual ambient concentration at or close to 0 ppb will be recorded as a small negative value. For the purpose of graphing data in this report, any average concentrations that are computed to be less than 0.0 ppb have been replaced with a value of 0.0 ppb.
- In addition, because of the large number of near 0.0 ppb measurements made for H_2S and SO_2, an additional quality assurance step was taken in the preparation of this final report. In order to guarantee that no gas from the calibration system would be mistaken for ambient air, an additional 5-minute observation was deleted from the data immediately following any calibration or span check or maintenance activity at the Project sites.
- Auto-GC data are sampled once an hour for a 40 minute sampling duration, after which the sample is analyzed for 46 hydrocarbon species, 27 of which were evaluated and reported on in this project. Each 40-minute sample average concentration is considered to

represent the average concentration for a full hour. Quality assurance runs on the auto-GCs consumed two to three hours of each day.

- Canister samples are taken by regulated mass flow meters for 20 minutes, with concentrations measured some days later in a laboratory at UT Austin. Often, the start of a canister sample has been recorded by hand on a log sheet, and found to have been entered a few minutes different than the recorded mass flow meter data, and sometimes different by an hour based on the operator's use of daylight savings time instead of standard time. Efforts have been made to correct the field time tagging in the canister database, but in some cases errors may exist.
- Because only a partial month and in some cases only a few days of data were collected in December 2004 for this project, many graphs in this report start with January 1, 2005. However, data from December 2004 have been examined and were used in assessing overall statistics for the project.

3.3 Using Wind Data with Pollutant Data

Each monitoring site collected both pollutant measurements and meteorological data including wind speed and wind direction. One way to use coincident wind direction measurements with the pollutant measurements is to graph the pollutant concentrations by the wind direction, so that both pollutant concentration and wind direction are continuous numeric values. A second approach is to calculate the average concentrations or other statistic by wind direction, in which case the average would be calculated for observations in a particular wind direction range. In this case the mean concentration is still a continuous numeric value, but the wind bins are discrete values. For example, one can specify distinct ranges of wind directions, say, 10 degree wind bins, centered at 0 degrees (>= 355 degrees, < 5 degrees), 10 degrees (>= 5, < 15), 20 degrees (>=15, < 25), etc. The resulting means may be examined to estimate roughly the upwind direction associated with the highest mean concentration, suggesting the direction of an emission source. An alternative approach to using mean concentration by wind direction bins is the Conditional Probability Function (CPF) method of counting the frequency with which a pollutant concentration is measured above a threshold value within a wind direction bin. Such a threshold value may be the overall 95th percentile value for that pollutant. In either the use of means by direction or CPF, the resulting graph can be smoothed to determine peak directionality. However, caution must be taken in assuming that wind direction measurements are exact representations of a straight-line path that an air parcel may have taken in reaching a monitoring site. In this report, several approaches are taken in using wind data with pollutant measurements.

3.4 Email Alerts

Described in Chapter 2 is a surface air parcel trajectory online tool that was integrated with an email alert system in which alerts were triggered by sustained elevated TNMHC or SO_2. Below in Table 3-3, page 3-6, is an example of an e-mail alert that was generated by an elevated SO_2 concentration measurement at the J. I. Haley CAMS 630 site in late 2013. The email alert lists the time and location of the measurement, the concentrations that triggered the alert with the alert threshold, the coincident wind speed and direction, and a list of known upwind industrial facilities (in this case only one). An example of the output from the online air parcel trajectory tool related to the email alert is shown in Figure 3-3, page 3-7.

Table 3-3. Email alert generated by elevated SO_2 measurement at J. I. Haley CAMS 630, 10/30/2013

From: the_denz@mail.utexas.edu
Sent: Wednesday, October 30, 2013 12:01 PM
To: Sullivan, David W;
Subject: (SERVER2) Corpus Christi Alert System Notice

The following alert has been received in the Corpus Christi Area:

emrs_low_alert_48355003742401_20131030_0755.txt

SO2 LOW trigger at site J.I. Hailey C630. No previous trigger.
63.84 >= 50.00 ppbV
WD = 139 degrees
WS = 11.4 mph
time of trigger 7:55 (CST) 2013.10.30
13:55 (UTC) 2013.10.30

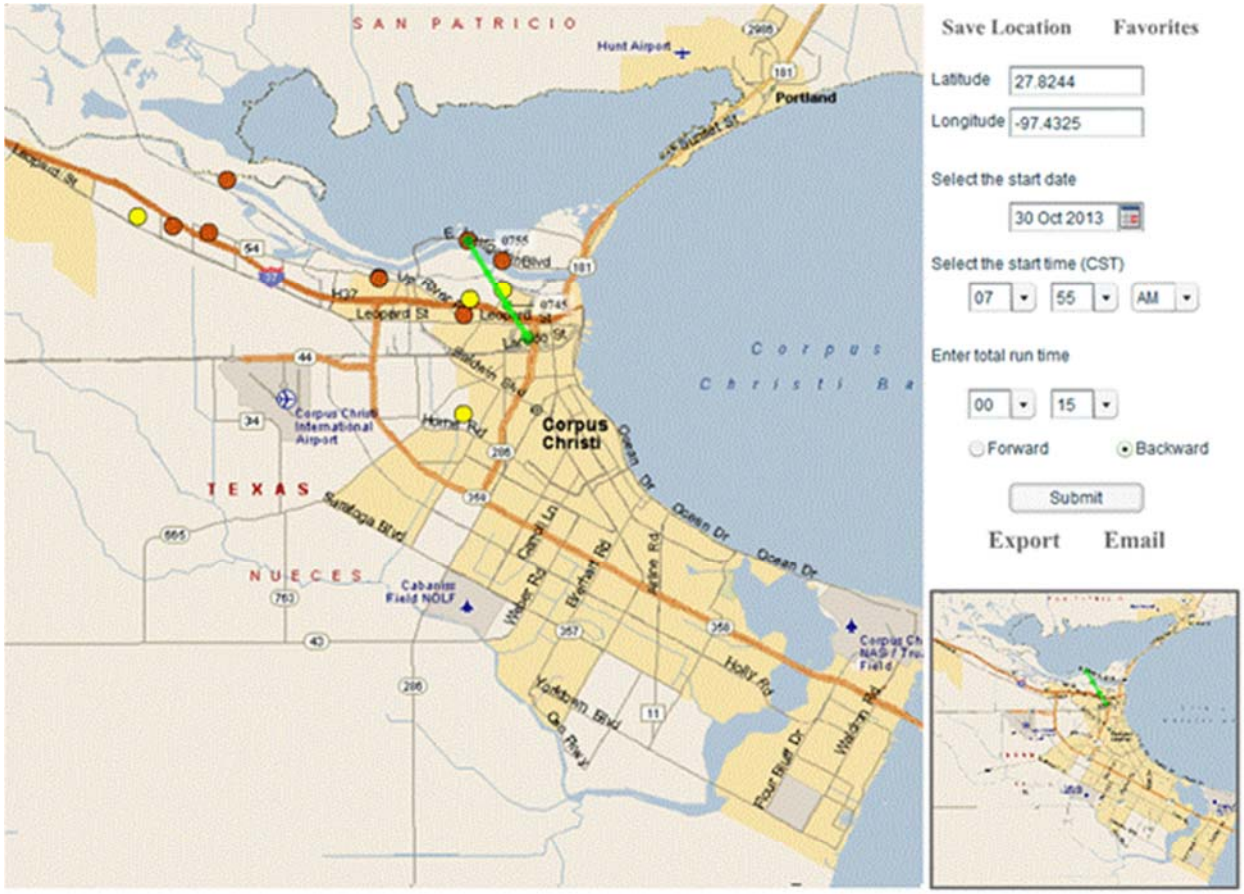
-97.421 | 27.807 | FLINT HILLS RESOURCES LP

To see the graphical output from the Corpus Christi Trajectory Tool of this alert click the following link:
Click Here

Click this link to go to the Alert Archive to view other alerts in the Corpus Christi area:
Click Here

Alert Troubleshooting Inquiry Form (for CEER Staff Only):
Click Here

Figure 3-3. Back trajectory associated with the alert on October 30, 2013, from JI Hailey CAMS 630



Alert ID: emrs_low_alert_48355003742401_20131030_0755

SO2 LOW trigger at site J.I. Hailey C630. No previous trigger.
53.84 >= 50.00 ppbV
WD = 139 degrees
WS = 11.4 mph
time of trigger 7:55 (CST) 2013.10.30
13:55 (UTC) 2013.10.30

3.5 Monitoring Results

In the following sections 3.5.1 through 3.5.7, data results from individual monitor stations are discussed. Section 3.5.8 describes how a network of monitors working together can provide more information.

3.5.1 Port Grain CAMS 629

Port Grain CAMS 629 Site Characteristics

The Port Grain site was located at 2001B East Navigation Blvd, Corpus Christi, TX 78402, at latitude 27º 49' 3" North (27.8175000º), longitude -97º 25' 11" West (-97.4197222º), and elevation 12.0 meters (m). The site was recorded with the EPA site number 483550036, and TCEQ CAMS number 629. It was activated on December 1, 2004, and began producing data later that month. The site was decommissioned on May 22, 2016. An aerial image of the site appears in Figure 3-4, below. The site was located in a large parking lot for a grain handling facility frequented by many heavy-duty trucks and exposed to emissions from ships, the rail line, and industrial facilities to the north and south. Figure 3-5, page 3-9, shows a higher altitude aerial image with both the Port Grain and the nearby J. I. Haley CAMS 630 site relative to the ship channel, roads, and industrial facilities. The two sites are 0.9 miles apart.

Figure 3-4. Port Grain aerial view from 250 m altitude

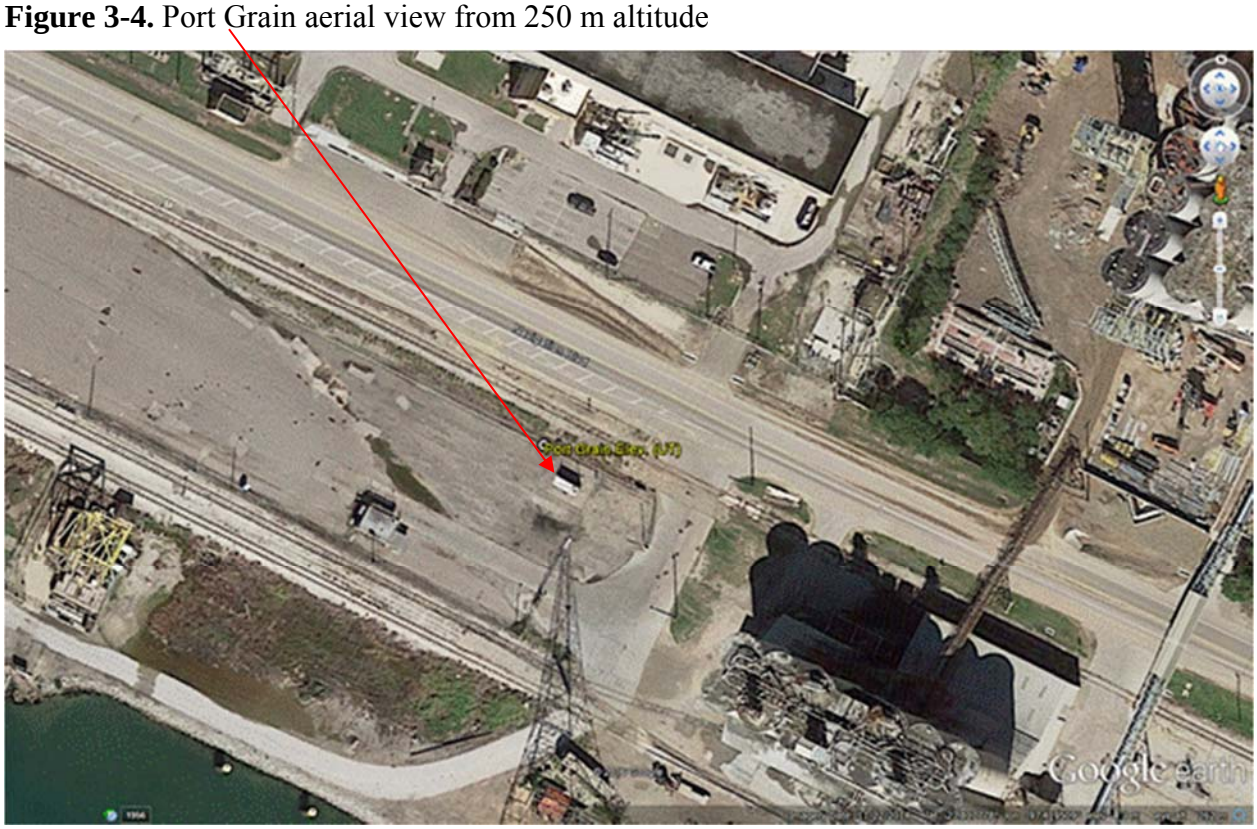


Figure 3-5. J. I. Hailey and Port Grain aerial view from 4 km altitude

Because of the location of the air monitoring shelter at the Port Grain site relative to the grain towers nearby (200 ft to the southeast) the winds blowing from the southeast were obstructed in reaching the site, thus compromising the ability of the site to accurately measure winds in all directions. Earlier, on page 3-3, Table 3-2 showed the mean wind speed at Port Grain was 8 mph compared to 11.3 mph at J. I. Haley, less than one mile away. Figure 3-6, below, shows a histogram of the wind directions measured over 11.5 years at Port Grain, reflecting the low incidence of wind directions around 120 – 150 degrees, which can be compared with Figure 3-1, page 3-2, for the composite winds in the area and with other sites' histograms later in this report. Figure 3-7, page 3-10, shows Port Grain's histogram of the wind speeds and can be compared to other sites' histograms later in this chapter.

Figure 3-6. Port Grain CAMS 629 wind direction distribution

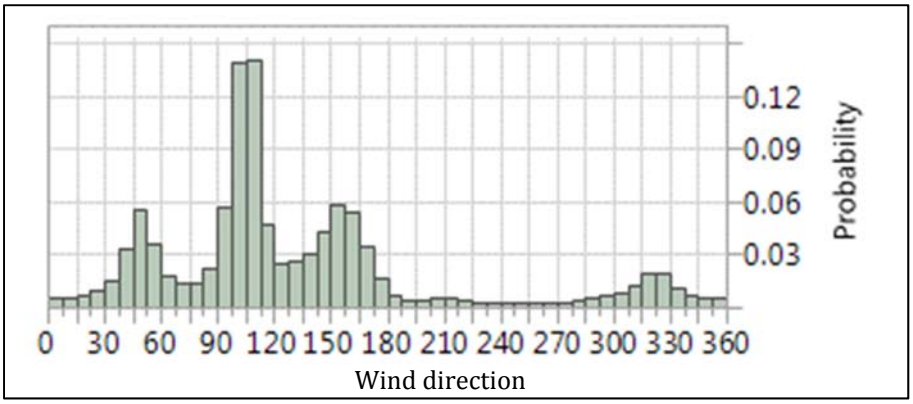
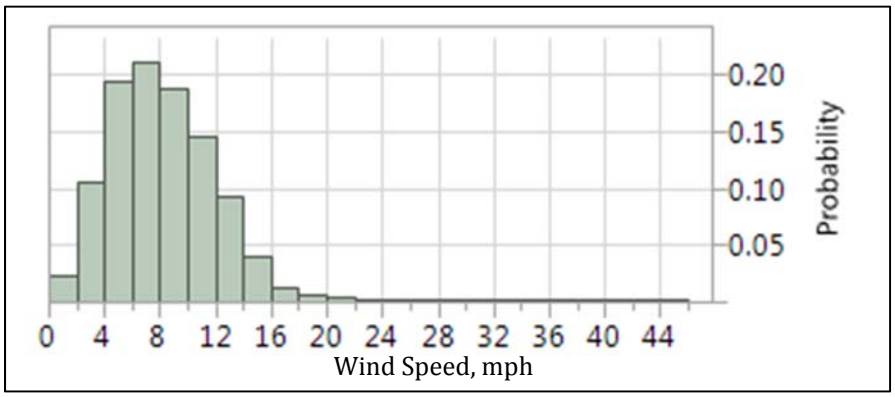


Figure 3-7. Port Grain CAMS 629 wind speed distribution



Port Grain CAMS 629 TNMHC

Figure 3-8, page 3-11, shows the time series for hourly TNMHC measurements from the Port Grain site. The data can be characterized as being highly skewed, wherein the large majority of measurements were less than 2,000 ppbC; a few values greater than 4,000 ppbC were measured, with only two since 2010. Figure 3-9, page 3-11, shows the time series for the mean TNMHC concentration by quarter of the year. What is interesting to note is that the concentrations declined from 2005 to 2011, but have flattened out since then for most quarters of the year. However, mean concentrations are statically significantly increasing during the fourth quarters of the years since 2009, and this trend produces an overall upward trend shown by the least squares curve fit to the data in Figure 3-9.

By merging the wind direction and TNMHC data, some clear information as to the direction to upwind sources appears. Figure 3-10, page 3-12, is a CPF contour plot of the frequency with which a concentration exceeds the 95th percentile 5-minute value over the period of monitoring. The image is color-coded for the highest frequency of exceedances of the 95th percentile 5-minute value of 372 ppbC. The figure shows that when monitoring began in 2004 and 2005, the highest concentrations came from the southwest direction. The legend in the figure shows that during 2004 and 2005, more than 70 percent of the time, when the wind blew from around 210 degrees, a value in the upper 5 percentile of measurements was recorded at this site. However, as shown earlier in Figure 3-6, this was a very low frequency of occurrence wind direction. Over time, the direction associated with the upper 5 percentile measurements shifted to the northwest through northeast, and although the frequency of the upper 5 percentile measurements was lower than the peaks from 2004 – 2006, the later high values came under more frequently occurring wind directions.

Figure 3-8. Time series for hourly TNMHC concentrations, ppbC units, Port Grain CAMS 629 site

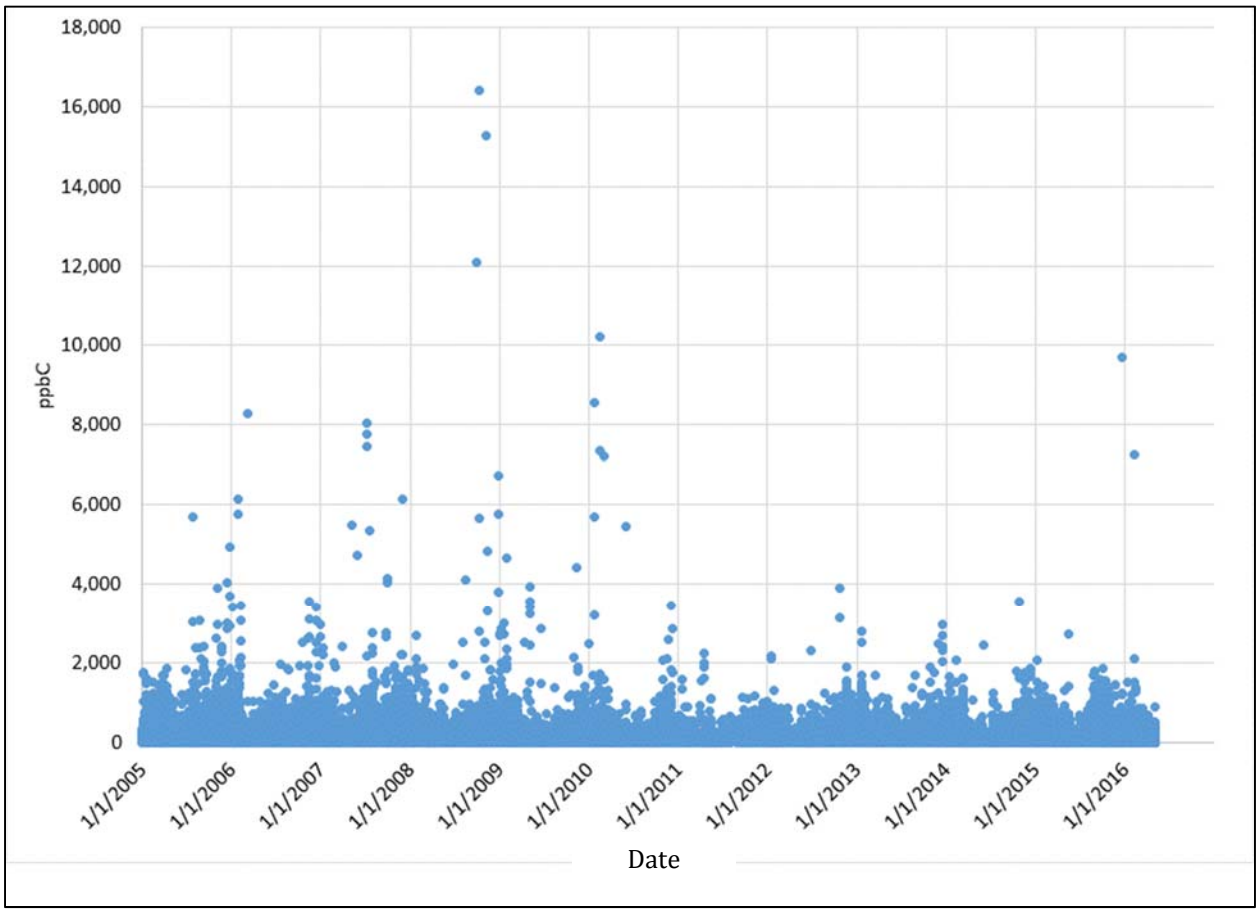


Figure 3-9. Quarterly mean TNMHC concentrations, ppbC units, Port Grain CAMS 629 site, with quadratic curve fit

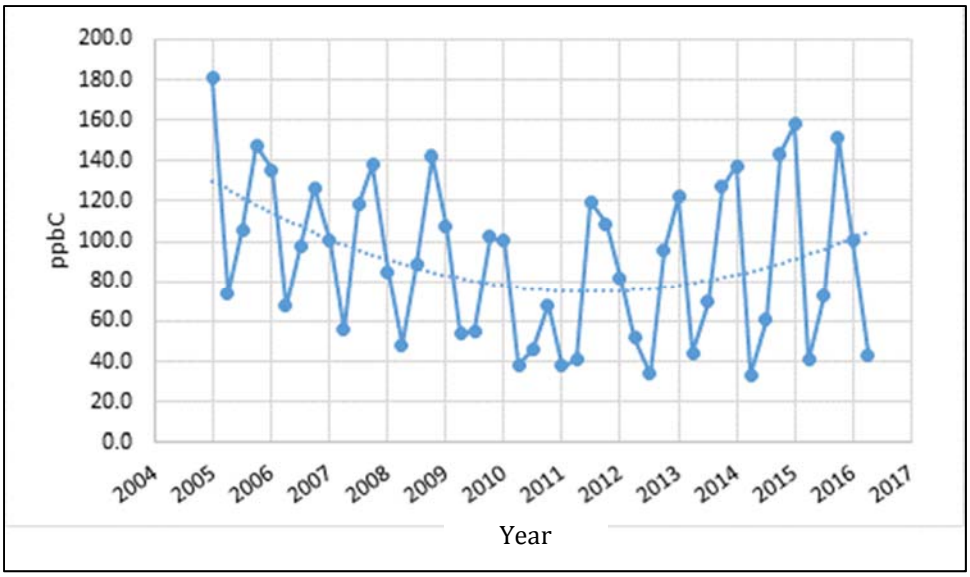
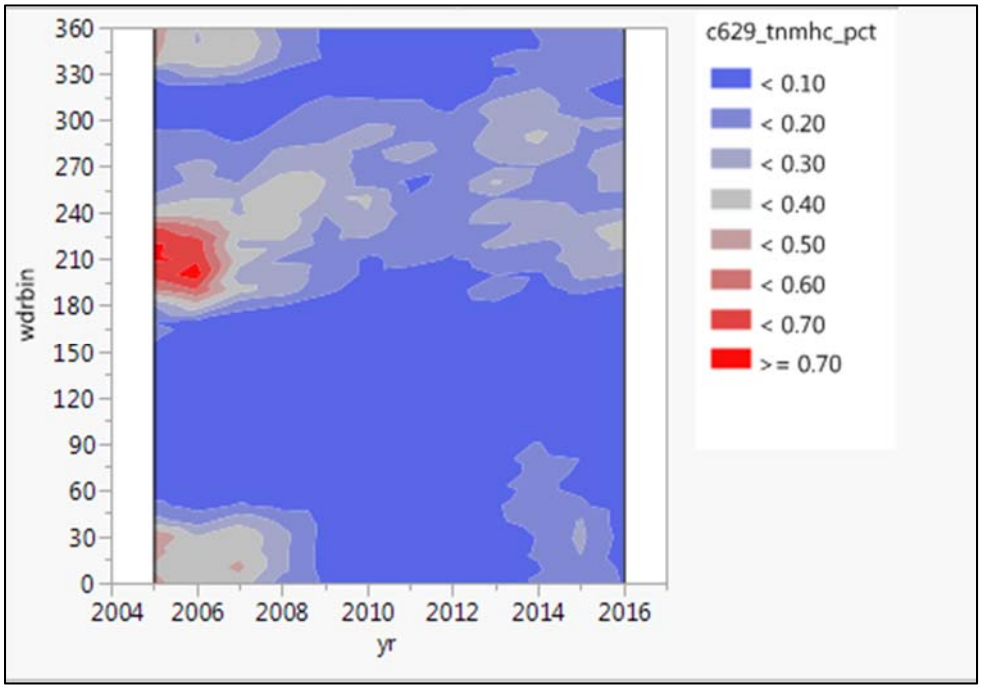


Figure 3-10. Contour plot of frequency Port Grain TNMHC concentrations exceed Port Grain 95th percentile 5-minute value over time



Port Grain CAMS 629 SO_2

In contrast to the more modest change in mean TNMHC concentrations at Port Grain, the SO_2 concentrations have significantly declined since monitoring began. Figure 3-11, page 3-13, shows the time series for hourly SO_2 measurements. There is very clearly a decrease in the frequency of elevated concentrations over time. As will be discussed later in this report, it is likely that reductions in the amount of sulfur in the fuel used in ships, coupled with other emission controls, have led to the decrease. Figure 3-12, page 3-13, shows a graph of the mean SO_2 concentration by quarter of the year. What cannot be seen clearly in Figure 3-11 is that in recent years, the large majority of measurements have been within the margin of error from 0.0 ppb, with only occasional measurements as high as 10 to 30 ppb. Thus, in Figure 3-12, the quarterly mean concentrations appear to bottom out close to 0 ppb.

Figure 3-13, page 3-14, is a CPF contour plot of the frequency with which an SO_2 concentration exceeds the 95th percentile 5-minute value over the period of monitoring. At Port Grain, only 5 percent of all 5-minute time period measurements were greater than 0.95 ppb. The image in Figure 3-13 is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows that when monitoring began in late 2004 and through 2005, the highest concentrations came from the southwest direction, as was the case with TNMHC. The legend in the figure shows that more than 70 percent of the time when the wind blew from the low frequency wind direction around 210 degrees, values in the highest 5 percentile of measurements were recorded, as was the case with TNMHC. Over the space of a few years the frequency of upper 5 percentile values declined.

Figure 3-11. Port Grain CAMS 629 SO_2 time series, Jan. 2005 – May 2016

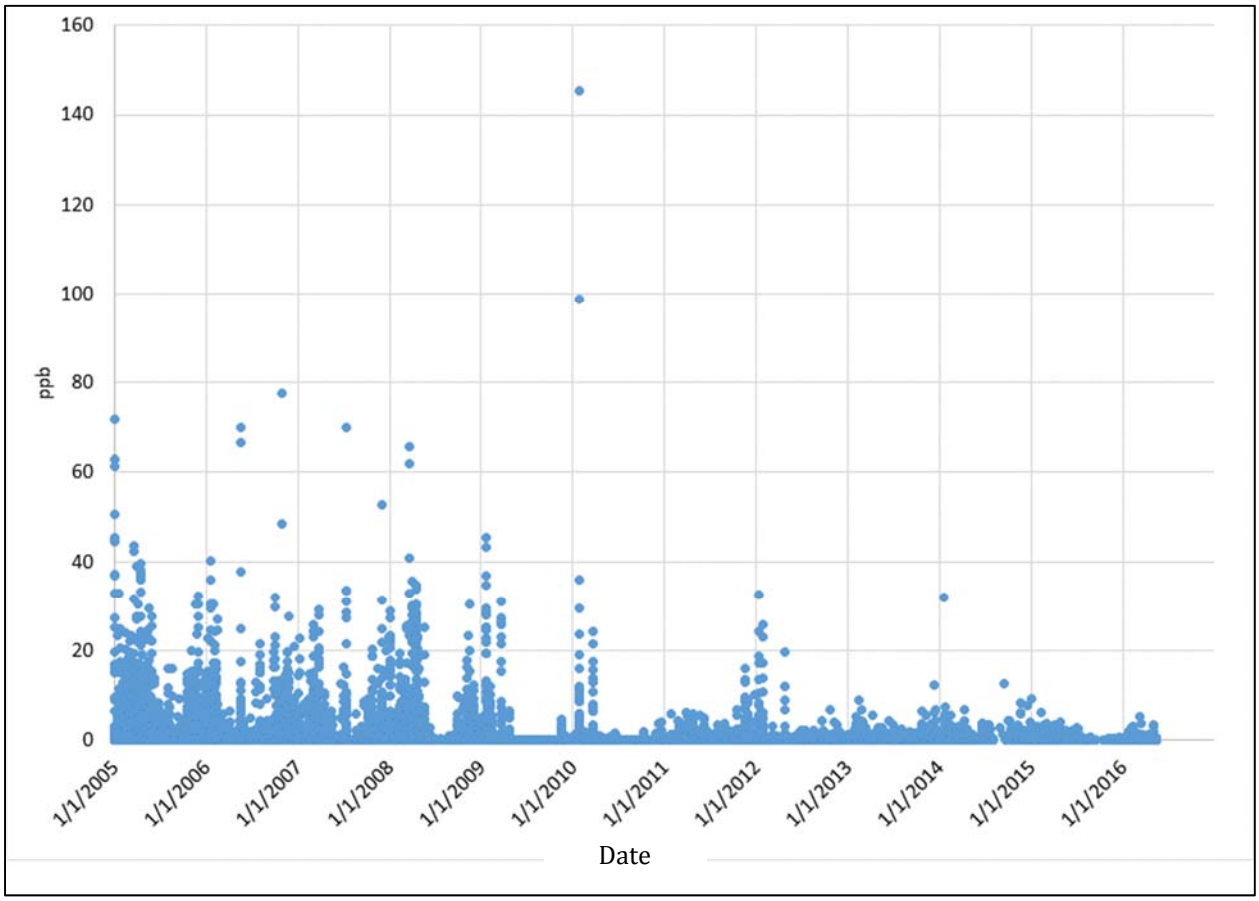


Figure 3-12. Port Grain CAMS 629 SO_2 quarterly mean concentrations, Jan. 2005 – May 2016

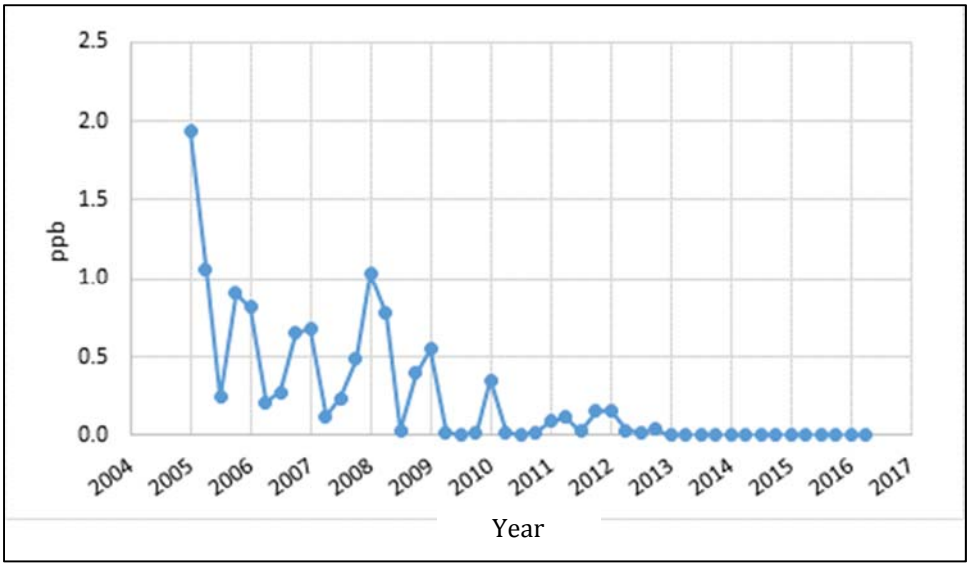
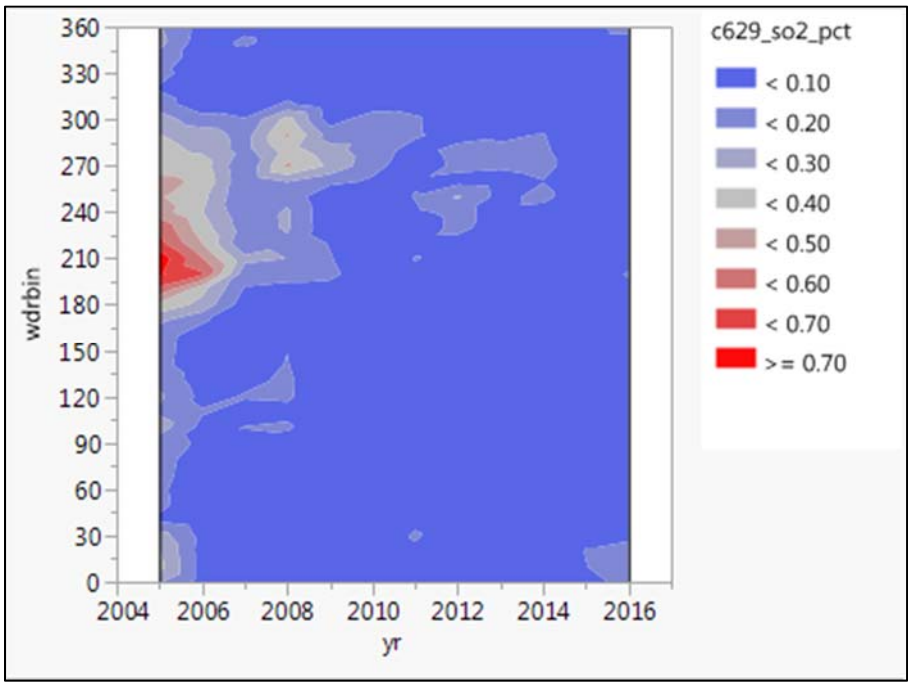


Figure 3-13. Contour plot of frequency that SO_2 concentrations exceeded the 95th percentile 5-minute value for SO_2 at Port Grain CAMS 629



Port Grain CAMS 629 H_2S

The third pollutant measured at the Port Grain site was hydrogen sulfide (H_2S). Concentrations of this pollutant have declined, but not to the near-0.0 ppb background conditions. Figure 3-14 page 3-15, shows the time series for hourly H_2S measurements. A significant outlier observation from January 13, 2005, makes it hard to detect a trend in Figure 3-14. The peak hour on January 13, 2005, measured an H_2S concentration of 183 ppb, and a close examination suggests this measurement was the result of a monitoring system malfunction (an unflagged calibration). The data are recast in Figure 3-15 page 3-16, without the outlier value. Figure 3-16, page 3-16, shows a graph of the mean H_2S concentration by quarter of the year. There has been a decrease in H_2S at the site, as shown in Figure 3-16, but not to 0.0 ppb background levels. The CPF contour plot in Figure 3-17, page 3-17, for the wind directions and time periods that H_2S concentration exceeded the 95th percentile 5-minute value of 1.3 ppb over the period of monitoring shows sustained elevated concentrations over the duration of the project in the low frequency southwesterly wind direction. Among all seven sites, when looking at the average H_2S concentration by wind direction, the Port Grain site had the highest average for a given wind direction – i.e., 4.6 ppb for winds directions between 220- 229.9 degrees.

Figure 3-14. Port Grain CAMS 629 Port Grain H_2S time series, Jan. 2005 – May 2016

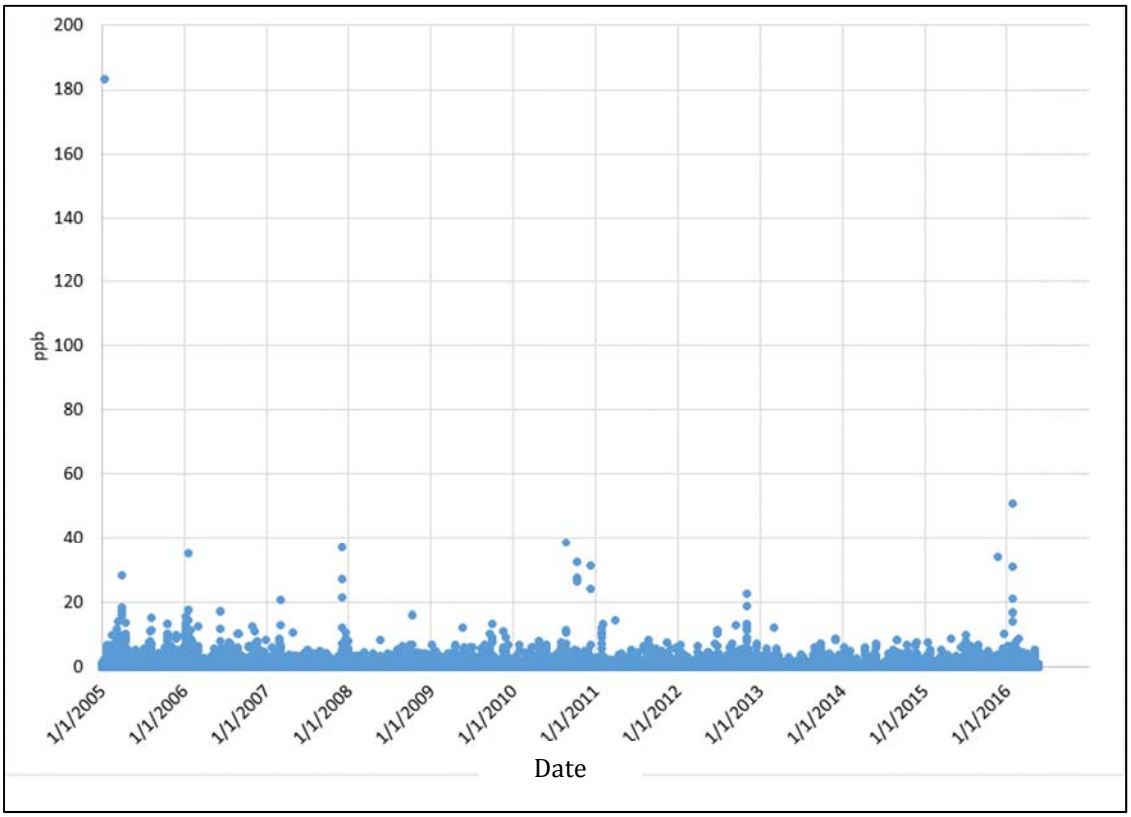


Figure 3-15. Port Grain CAMS 629 Port Grain H_2S time series, Jan. 2005 – May 2016, sans one outlier

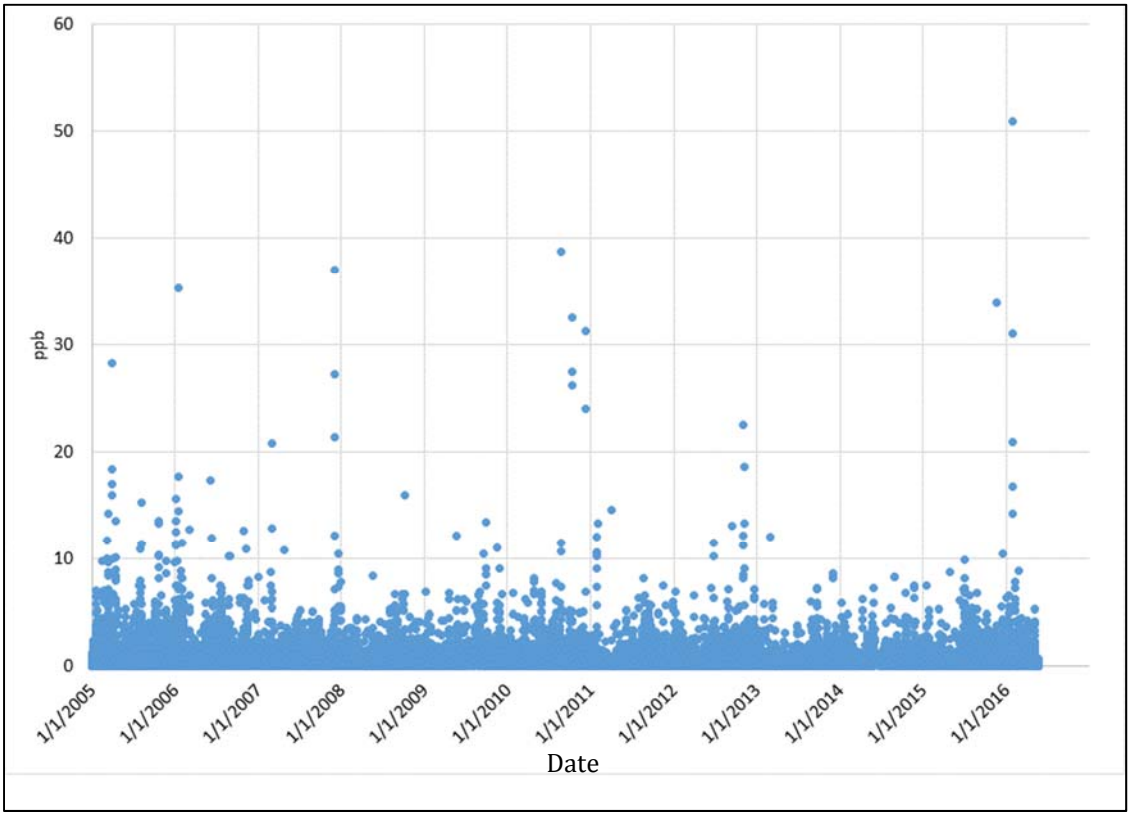


Figure 3-16. Port Grain CAMS 629 Port Grain H_2S quarterly mean concentrations, Jan. 2005 – May 2016

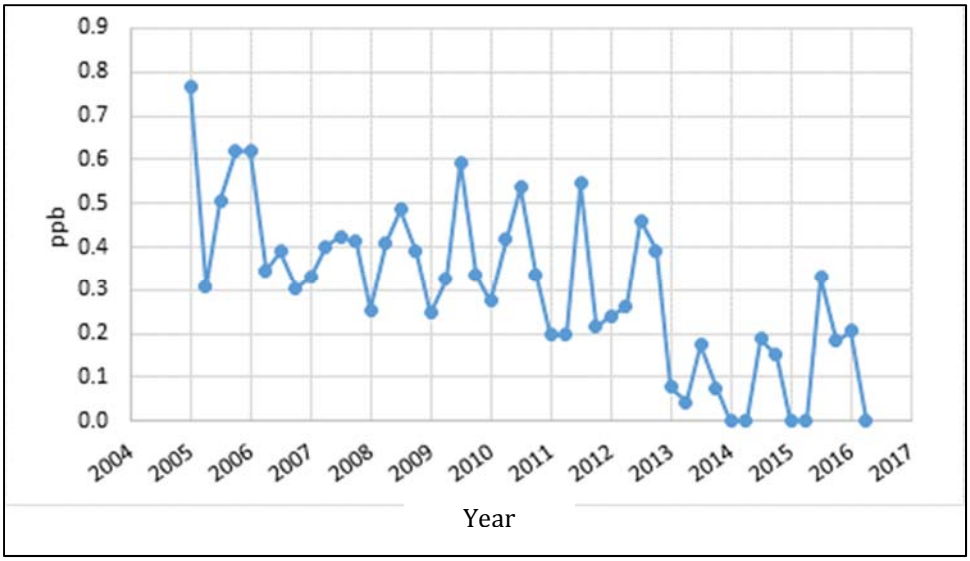
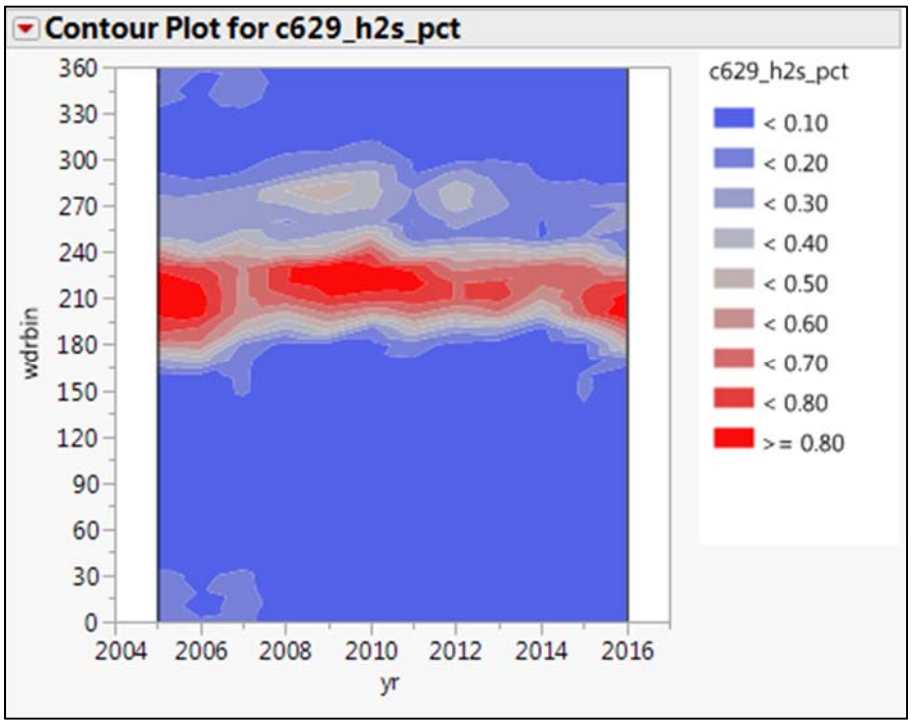


Figure 3-17. Contour plot of frequency that H_2S concentrations exceeded the 95th percentile 5-minute value for H_2S at UT CAMS 629 Port Grain



3.5.2 J. I. Hailey CAMS 630

J. I. Hailey CAMS 630 Site Characteristics

The J. I. Hailey site was located at 2702B East Navigation Blvd, Corpus Christi, TX 78402, at latitude 27º 49' 28" North (27.8244º), longitude -97º 25' 57" West (-97.4325º), and elevation 12.0 m. The site was recorded with the EPA site number 483550037, and TCEQ CAMS number 630. It was activated on November 30, 2004, and began producing data in mid-December. The site was decommissioned on May 22, 2016. An aerial image of the site appears in Figure 3-18, below. The site was located just off the Fulton Turnpike, with exposure to the south to docks and refineries, and exposure to Nueces Bay to the north. Figure 3-19, page 3-19, shows a higher altitude aerial image with both the J. I. Haley and the nearby Port Grain CAMS 629 site relative to the ship channel, roads, industrial facilities, and the Nueces Bay. As was noted earlier in the report, the two sites are 0.9 miles apart.

As was noted earlier, the site is generally unobstructed with regard to wind flow. Figure 3-20, page 3-19, shows a histogram of the wind directions measured over 11.5 years at J. I. Hailey. Figure 3-21, page 3-20, shows J. I. Hailey's histogram of the wind speeds. As was noted earlier in the report, the mean wind speed at J. I. Haley was 11.3 mph, which was the highest average among the Project's and long-running TCEQ monitoring sites.

Figure 3-18. J. I. Hailey aerial view from 250m altitude

Figure 3-19. J. I. Hailey and Port Grain aerial view from 4 km altitude

Figure 3-20. J.I. Hailey CAMS 630 wind direction distribution

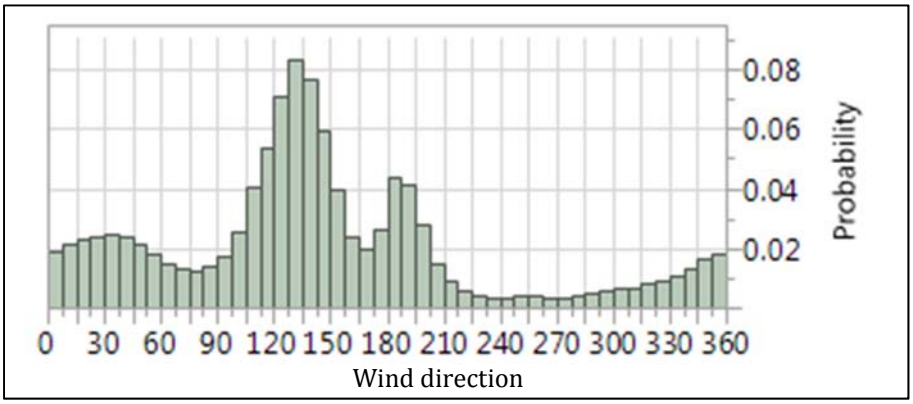
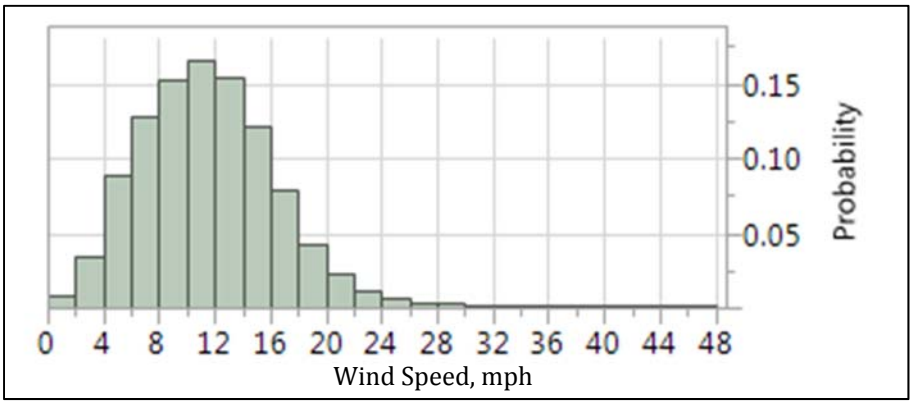


Figure 3-21. J.I. Hailey CAMS 630 wind speed distribution



J. I. Hailey CAMS 630 TNMHC

Figure 3-22, page 3-21, shows the time series for hourly TNMHC measurements from the J. I. Hailey site. In the first years of operating the site, TNMHC concentrations were cropped at 10,000 ppbC. As this level was hit several times, the cropping was lifted, and as a result, one-hour concentrations over 16,000 ppbC have been measured at the site. Figure 3-23, page 3-21, shows the time series for the mean TNMHC concentration by quarter of the year. As was observed with the Port Grain site, mean quarterly concentrations declined from 2005 to 2011, but have flattened out since then for most quarters of the year, with mean concentrations increasing (regression p-value = 0.06), during the fourth quarters of the years since 2009.

Figure 3-24, page 3-22, is a CPF contour plot of the frequency with which a TNMHC concentration exceeds the 95th percentile 5-minute value of 447 ppbC over the period of monitoring. The image is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows that when the upper 5-percentile highest concentrations were made, winds were generally from the southwest through northwest direction range, and these conditions persisted into 2016. The legend in the figure shows that in recent years more than 40 percent of the time that the wind blew from close to 240 or 310 degrees, a value in the upper 5 percentile of measurements from this site was recorded.

Figure 3-22. Time series for hourly TNMHC concentrations, ppbC units, J. I. Hailey CAMS 630 site

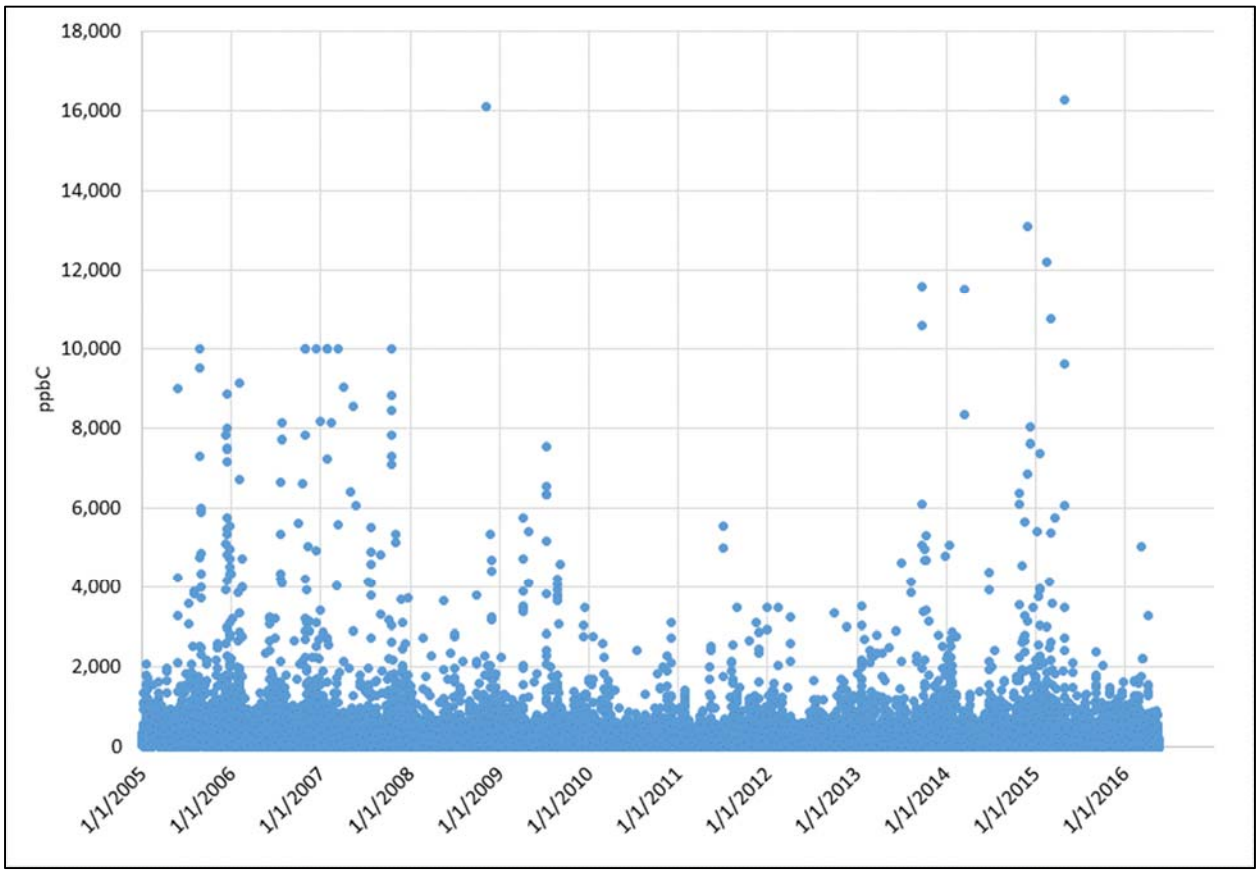


Figure 3-23. Quarterly mean TNMHC concentrations, ppbC units, J. I. Hailey CAMS 630, with quadratic curve fit

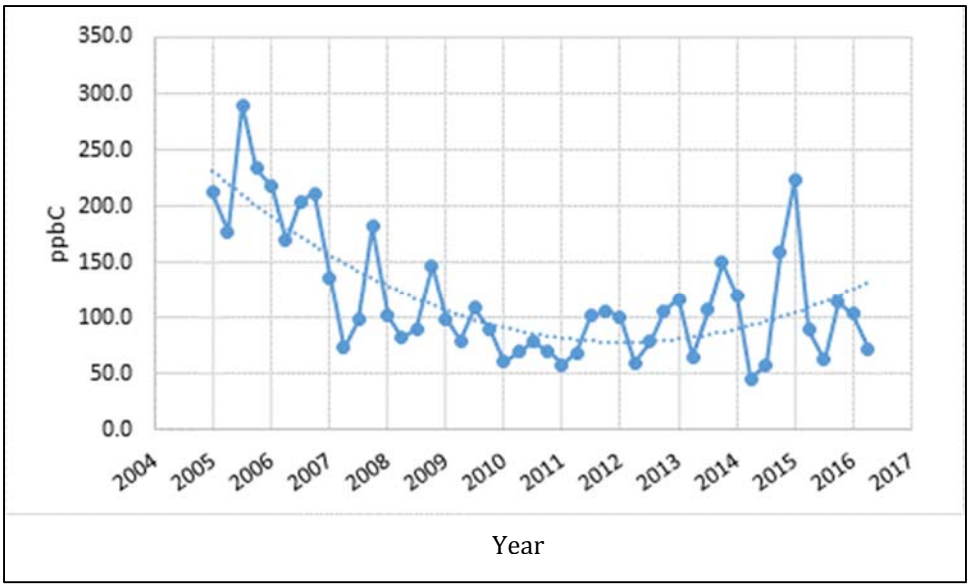
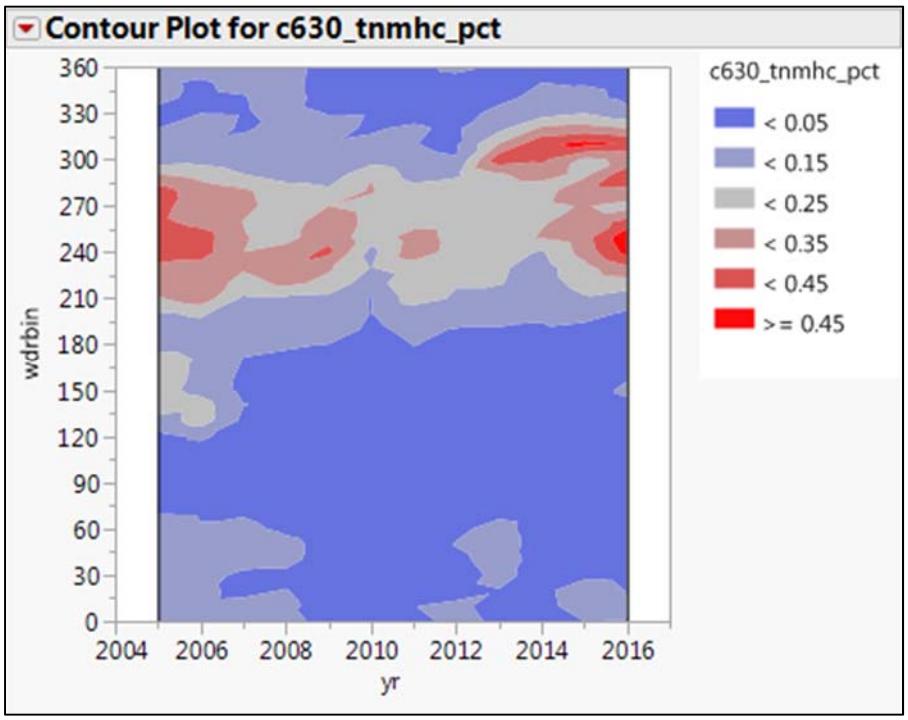


Figure 3-24. Contour plot of frequency that TNMHC concentrations exceeded the 95th percentile 5-minute value for TNMHC at J.I. Hailey CAMS



J. I. Hailey CAMS 630 SO_2

At J. I. Hailey, the SO_2 concentrations have significantly declined since monitoring began; when the project began, the J. I. Hailey site recorded the highest SO_2 concentrations in the region, and among the highest in the State of Texas. Figure 3-25, page 3-23, shows the time series for hourly SO_2 measurements. There is very clearly a decrease in the frequency of elevated concentrations over time. A set of joint investigations by UT Austin and the TCEQ showed that the likely cause of reductions in SO_2 concentrations were the reductions in the amount of sulfur in the fuel used in ships, coupled with other emission controls. Figure 3-26, page 3-23, shows a graph of the mean SO_2 concentration by quarter of the year. Mean concentrations are close to 0.0 ppb in recent quarters.

Figure 3-27, page 3-24, is a CPF contour plot of the frequency with which an SO_2 concentration exceeds the 95th percentile 5-minute value over the period of monitoring. At J. I. Hailey, only 5 percent of all 5-minute time scale SO_2 measurements were greater than 3.4 ppb. The image in Figure 3-27 is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows that when monitoring began in late 2004 and through 2005, the highest concentrations came from the southwest direction. Over the space of a few years the frequency of upper 5 percentile values significantly declined.

Figure 3-25. J.I. Hailey CAMS 630 SO_2 time series, Jan. 2005 – May 2016

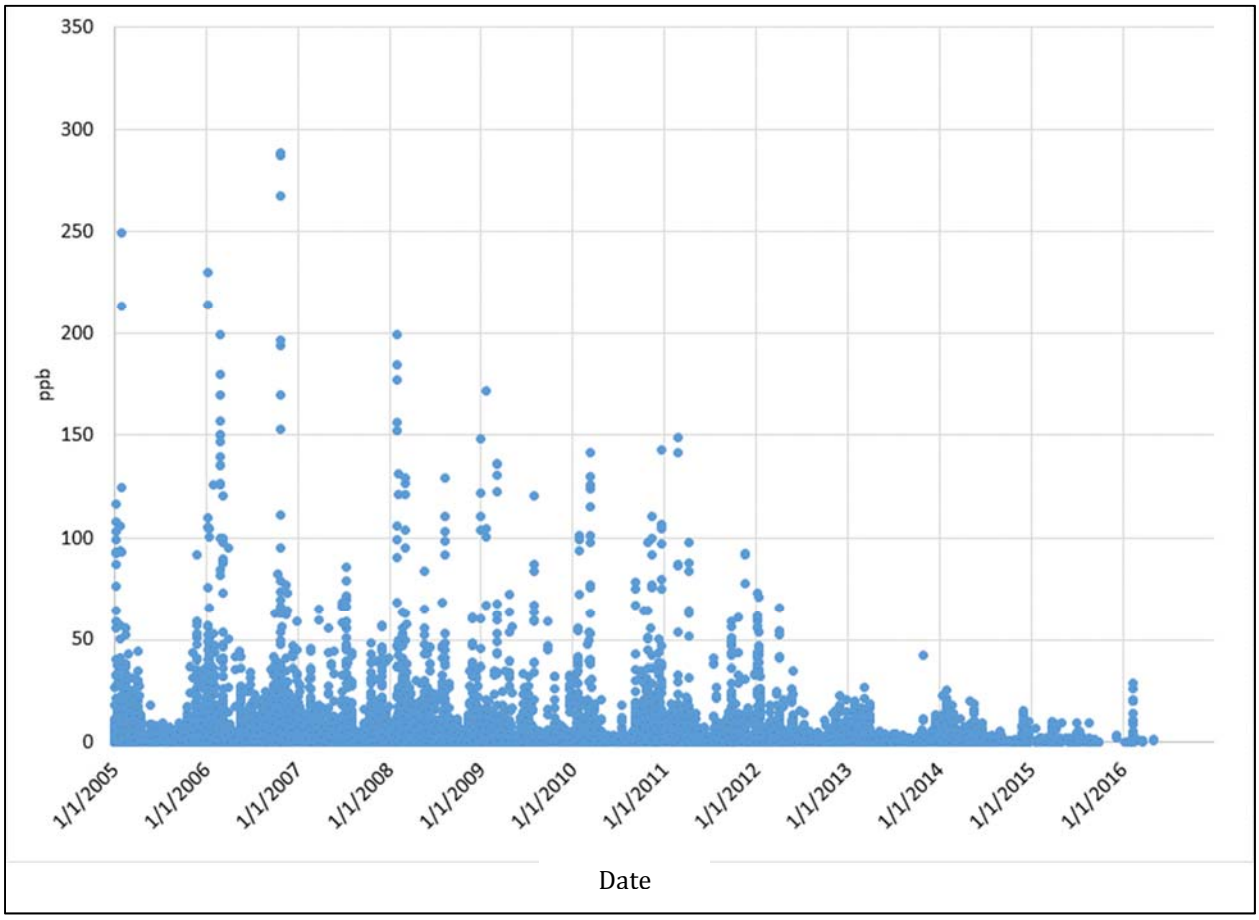


Figure 3-26. J.I. Hailey CAMS 630 SO_2 quarterly mean concentrations, Jan. 2005 – May 2016

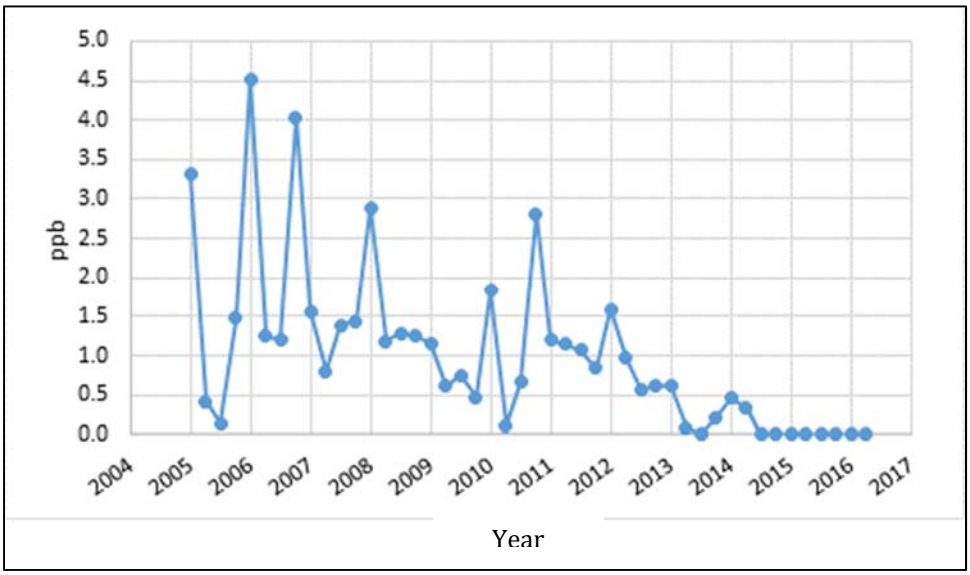
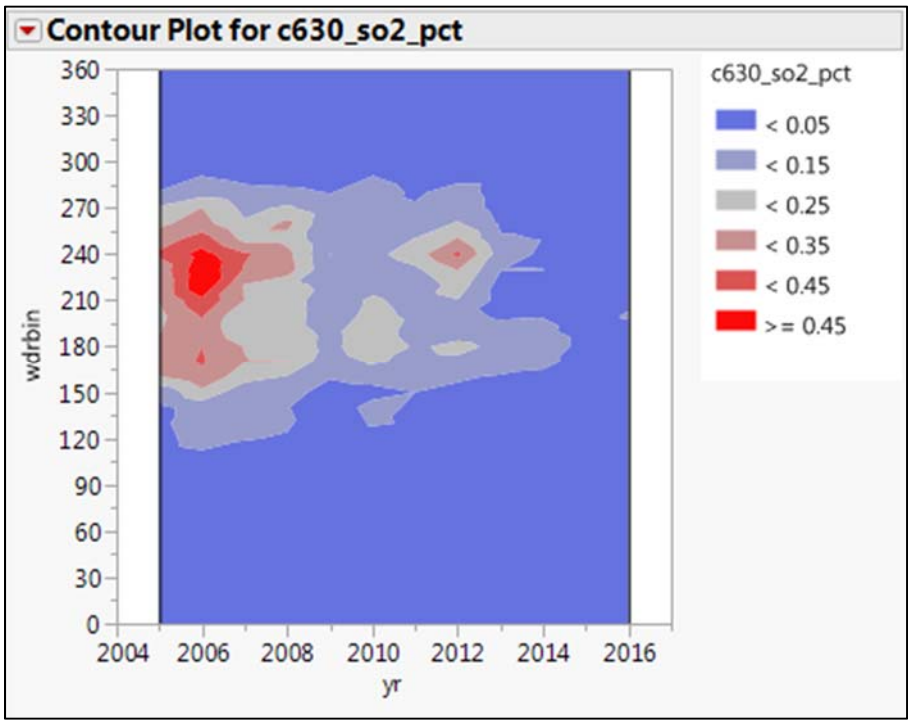


Figure 3-27. Contour plot of frequency that SO_2 concentrations exceeded the 95th percentile 5-minute value for SO_2 at J.I. Hailey CAMS 630



J. I. Hailey CAMS 630 H_2S

The third pollutant measured at the J. I. Hailey site was hydrogen sulfide (H_2S). Concentrations of this pollutant have declined, but not to the near-0.0 ppb background conditions. Figure 3-28, page 3-25, shows the time series for hourly H_2S measurements. A significant set of outlier observations in July 27 – 28, 2007, makes it hard to detect a trend in Figure 3-28. On the evening of July 27, 2007, under southerly winds, H_2S concentrations reached 513 ppb, coincident with TNMHC concentrations cropped at 10,000 ppbC. Exceedances of the TCEQ's 80 ppb rolling 30-minute standard occurred over 103 of 165 rolling 30-minute periods from 18:45 on July 27 to 8:30 CST on July 28, 2007.

The J. I. Hailey site H_2S data are recast in Figure 3-29, page 3-26, without the July 27-28, 2007, data exceeding 100 ppb. Figure 3-30, page 3-26, shows a graph of the mean H_2S concentration by quarter of the year. There has been a decrease in H_2S at the site, as shown in Figure 3-30, page 3-27, but not to 0.0 background levels. The CPF contour plot in Figure 3-31 for the wind directions and time periods that H_2S concentration exceeded the 95th percentile 5-minute value of 2.3 ppb over the period of monitoring shows sustained elevated concentrations over the duration of the project in the low frequency of occurrence southwesterly wind direction.

Figure 3-28. J.I. Hailey CAMS 630 H_2S time series, Jan. 2005 – May 2016

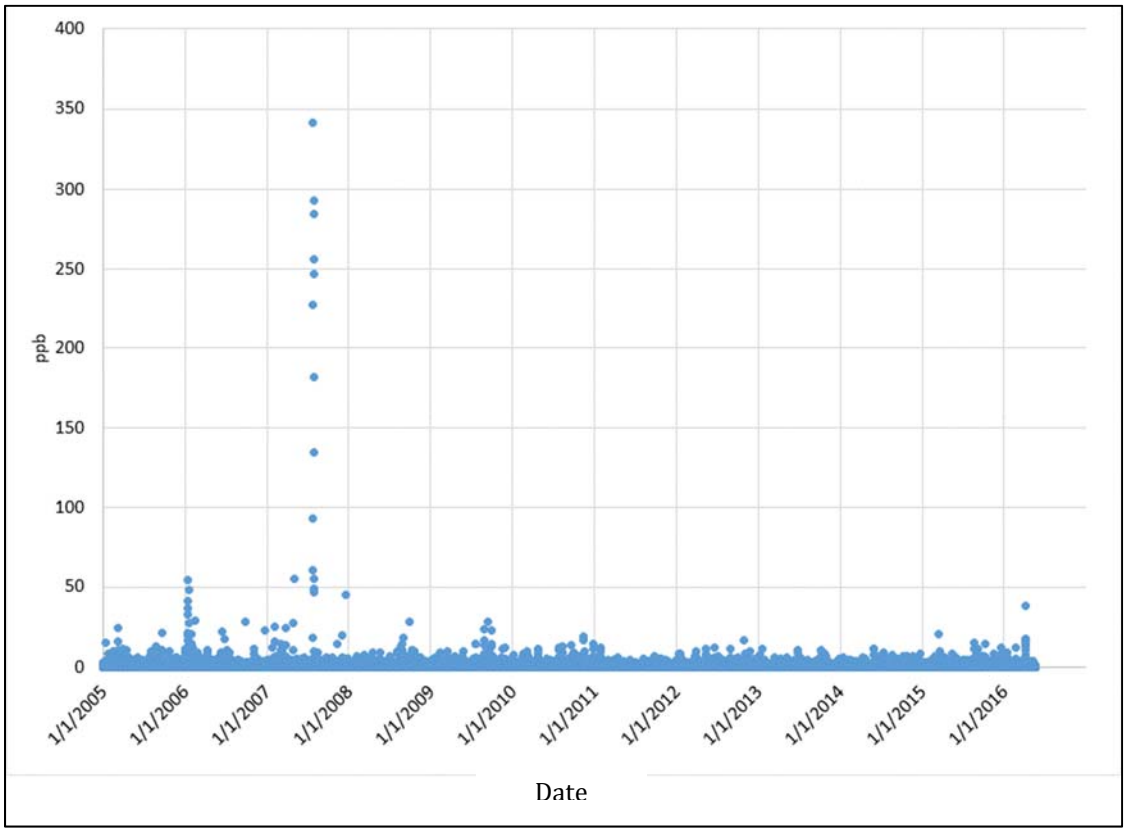


Figure 3-29. J.I. Hailey CAMS 630 H_2S time series, Jan. 2005 – May 2016 sans July 27-28, 2007, values greater than 100 ppb

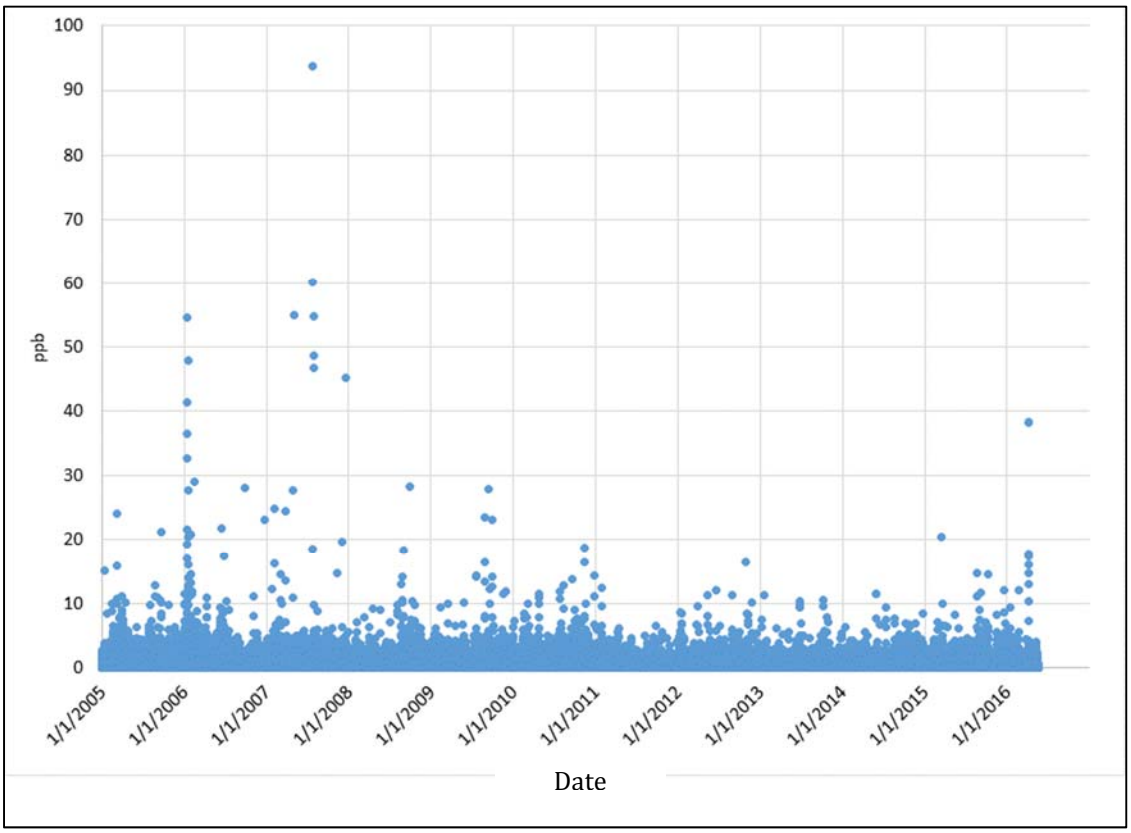


Figure 3-30. J.I. Hailey CAMS 630 H_2S quarterly mean concentrations, Jan. 2005 – May 2016

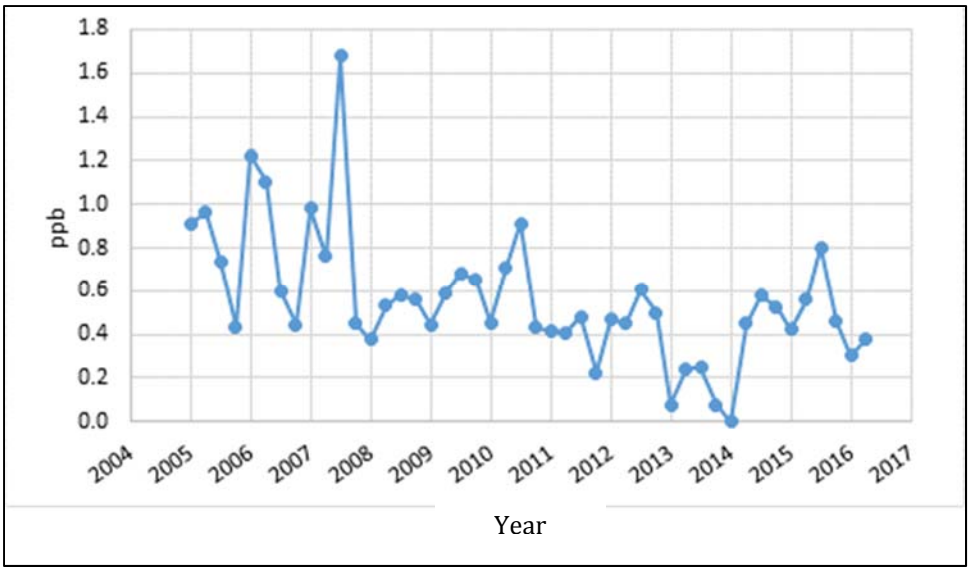
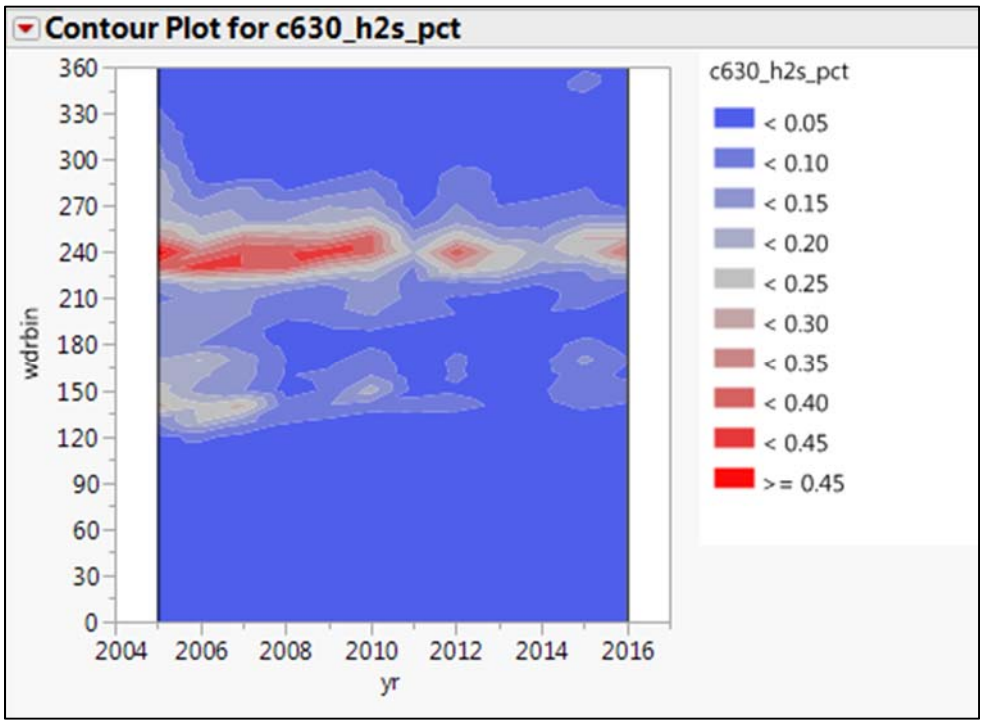


Figure 3-31. Contour plot of frequency that H_2S concentrations exceeded the 95th percentile 5-minute value for H_2S at J.I. Hailey CAMS 630



In part because of its excellent exposure to surrounding land uses, and in part because the site was well situated with regard to emissions sources, the J. I Hailey CAMS 630 site was the subject of several case studies over the course of the project. Three examples are provided below.

Case Study November 28, 2014, J. I. Hailey CAMS 630

Figure 3-32, on page 3-28, shows the time series of five-minute time interval data collected at J. I. Hailey CAMS 630 on the morning of November 28, 2014, for wind direction (WDR), TNMHC, methane, and canister pressure and mass flow. The graph has an arrow and label indicating when the canister sample was taken. The graph shows that TNMHC and methane concentrations rose rapidly around 6:00 CST with winds from the west. After sustained elevated concentrations had been measured, a canister was triggered at 6:50 CST. Figure 3-33, page 3-29, shows a surface back-trajectory begun at JIH at 6:45 CST and extending back to the west and south. The back trajectory suggests that the air reaching the site had passed over docks and the industrial area southwest across the ship channel. The coincident increase in methane with TNMHC suggests that natural gas was a component of the species measured. Figure 3-34, page 3-29, shows the mix of species from the canister analysis. The mix of the most prominent species – ethane, propane, n-butane, iso-butane, n-pentane, and iso-pentane – represents the mix typically associated with natural gas. Data in this bar graph are in ppbC units, so that the concentrations can be added together to compare with the coincident TNMHC concentrations. Comparisons with air monitoring comparative values (AMCVs) are done after converting to ppbV units. No values exceeded an AMCV.

Figure 3-32. November 28, 2014, J. I. Hailey CAMS 630 five-minute time interval data

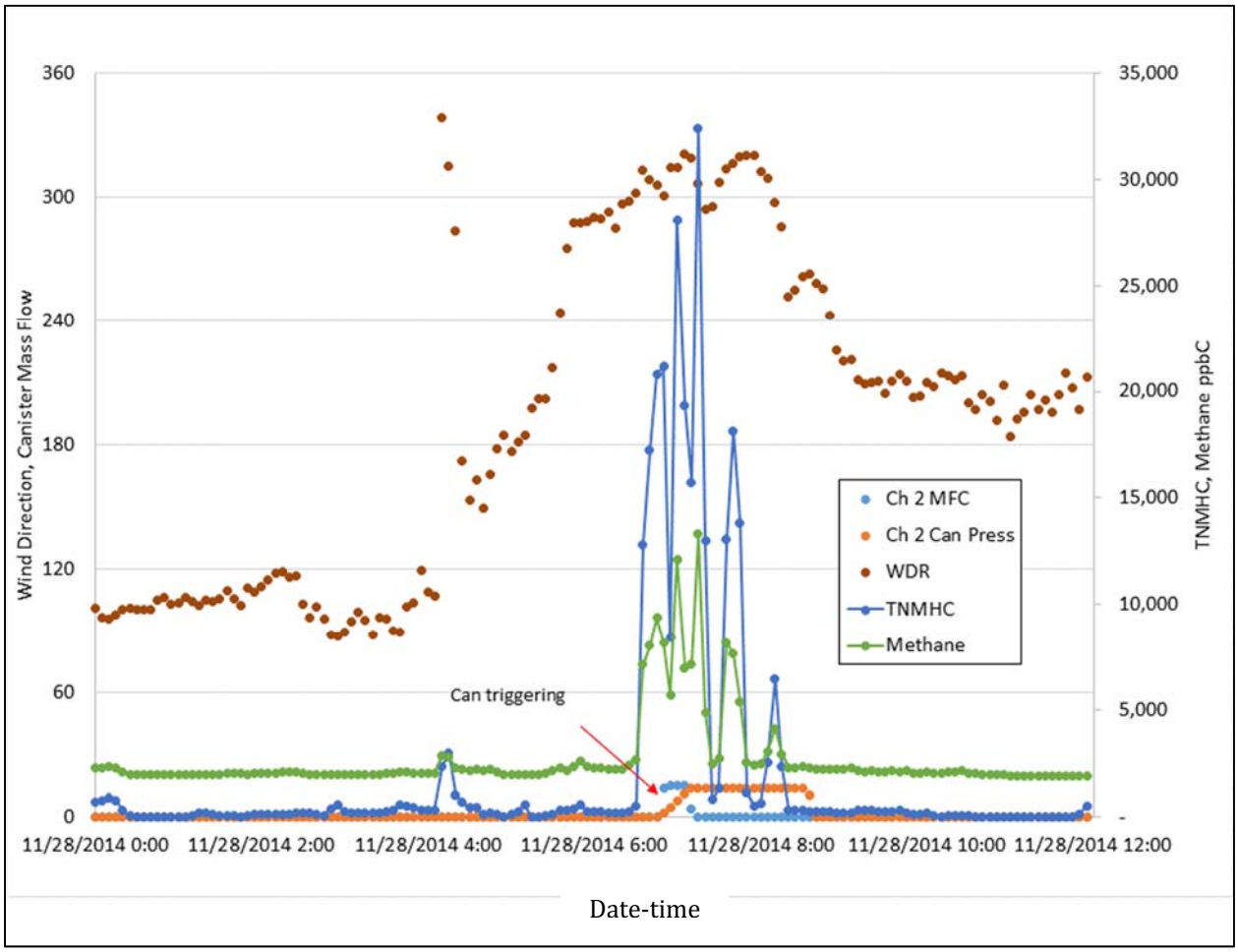


Figure 3-33. November 28, 2014, J. I. Hailey CAMS 630 surface back-trajectory begun at 6:45 CST and extending back to the west and south

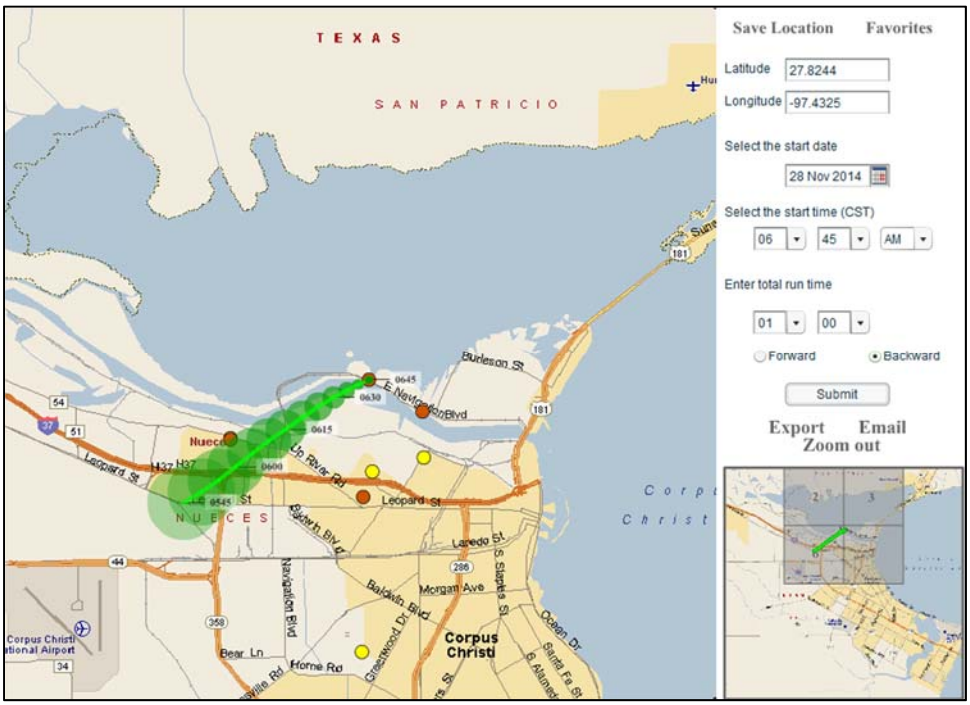
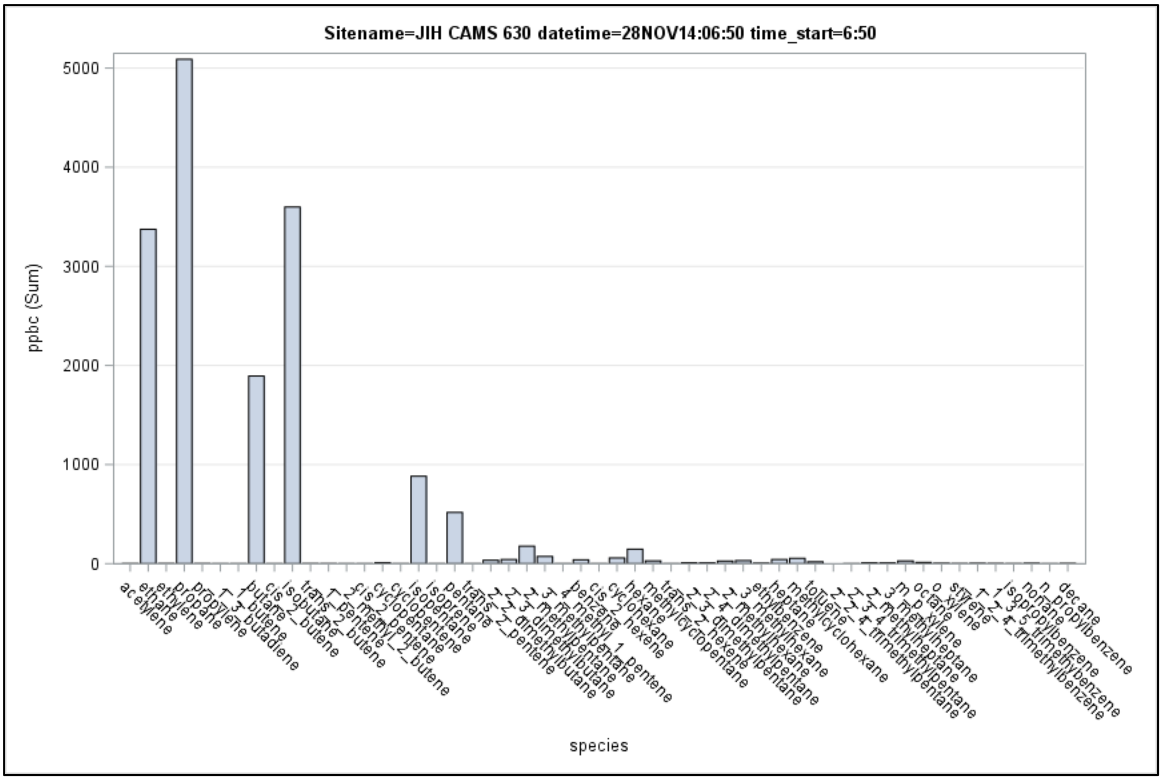


Figure 3-34. November 28 J. I. Hailey CAMS 630 canister mix of species from laboratory analysis



Case Study January 18, 2015, J. I. Hailey CAMS 630

Figure 3-35, page 3-31, shows the time series of five-minute time interval data collected at J. I. Hailey CAMS 630 overnight on January 17 – 18, 2015, for wind direction (WDR), TNMHC, methane, and canister pressure and mass flow. The graph has an arrow and label indicating when the canister sample was taken. The graph shows that TNMHC concentrations rose rapidly around 23:45 CST on January 17 with winds from the west. After sustained elevated concentrations had been measured, a canister was triggered a minute after midnight CST. Figure 3-36, page 3-32, shows a surface back-trajectory begun at JIH at midnight CST and extending back to the west and south. The back trajectory suggests that the air reaching the site had passed over docks and the industrial area southwest across the ship channel. This trajectory looks very much like the previous case study back trajectory in Figure 3-33, page 3-29. In this case, there was not a significant coincident increase in methane with TNMHC. Figure 3-37, page 3-32, shows the mix of species from the canister analysis. The large majority of material in the canister was the single species toluene. The air monitoring comparison value for toluene is 4000 ppbV. The concentration shown in Figure 3-37 is 1,037 ppbC, which is 148 ppbV. However, one can observe that the canister sample was taken after the peak TNMHC concentration at 23:50 CST of 10,588 ppbC. If this were 100 percent toluene, the resulting ppbV value would be 1,513 ppbV, which is still well below the AMCV.

Figure 3-35. January 17 – 18, 2015, J. I. Hailey CAMS 630 five-minute time interval data

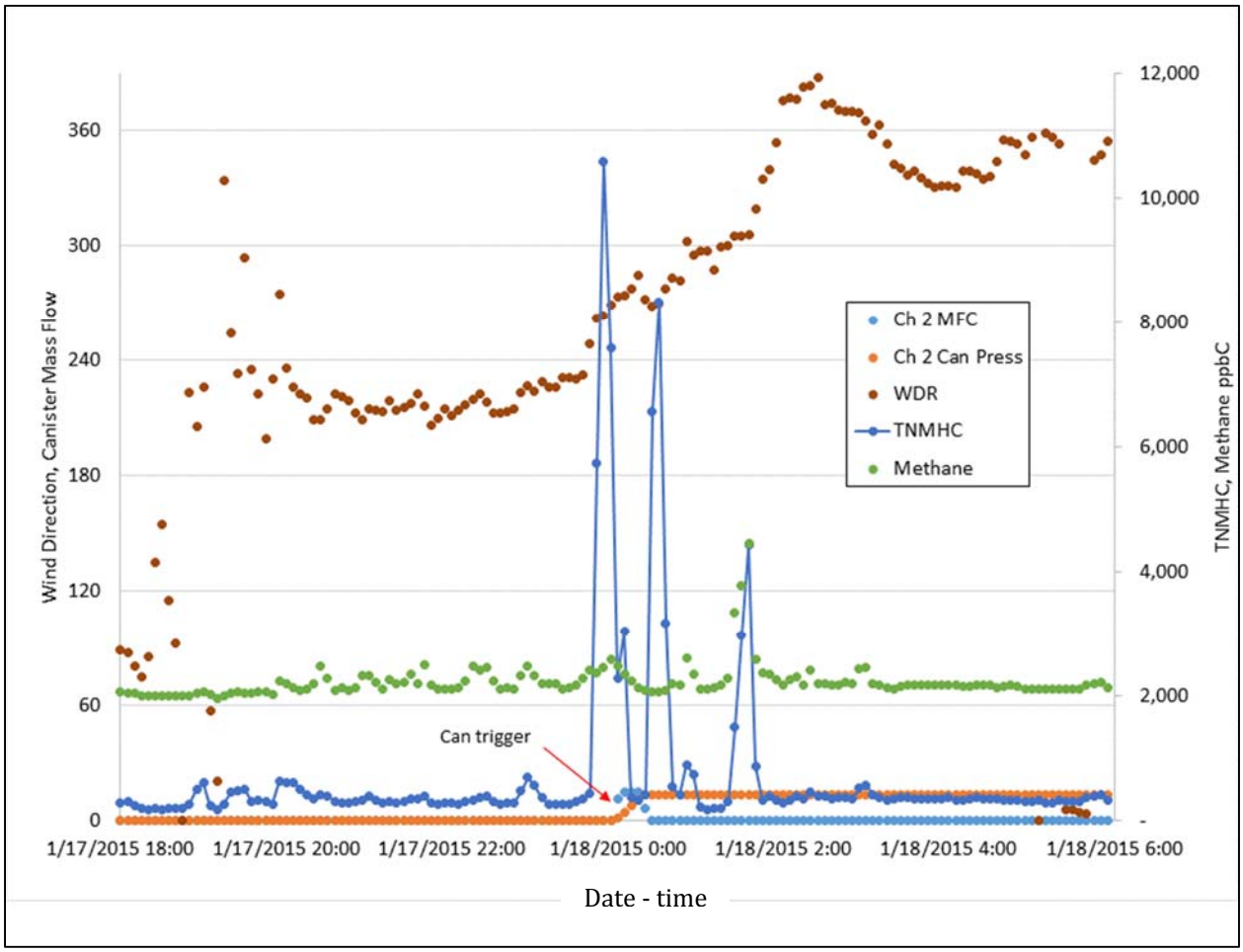


Figure 3-36. January 18, 2015, J. I. Hailey CAMS 630 surface back-trajectory begun at midnight CST and extending back to the west and south

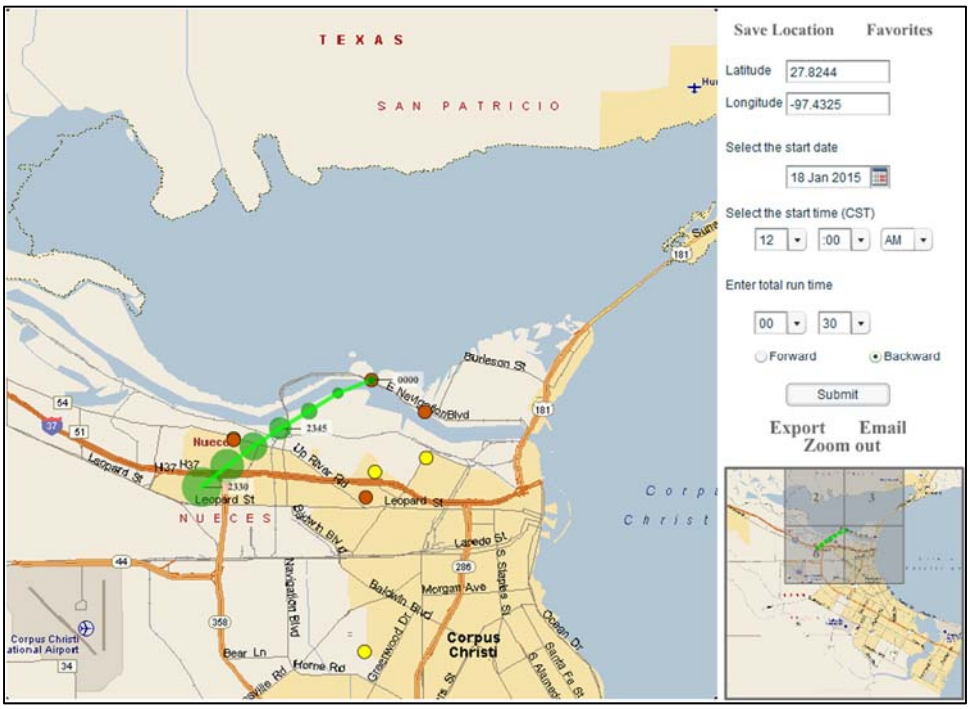
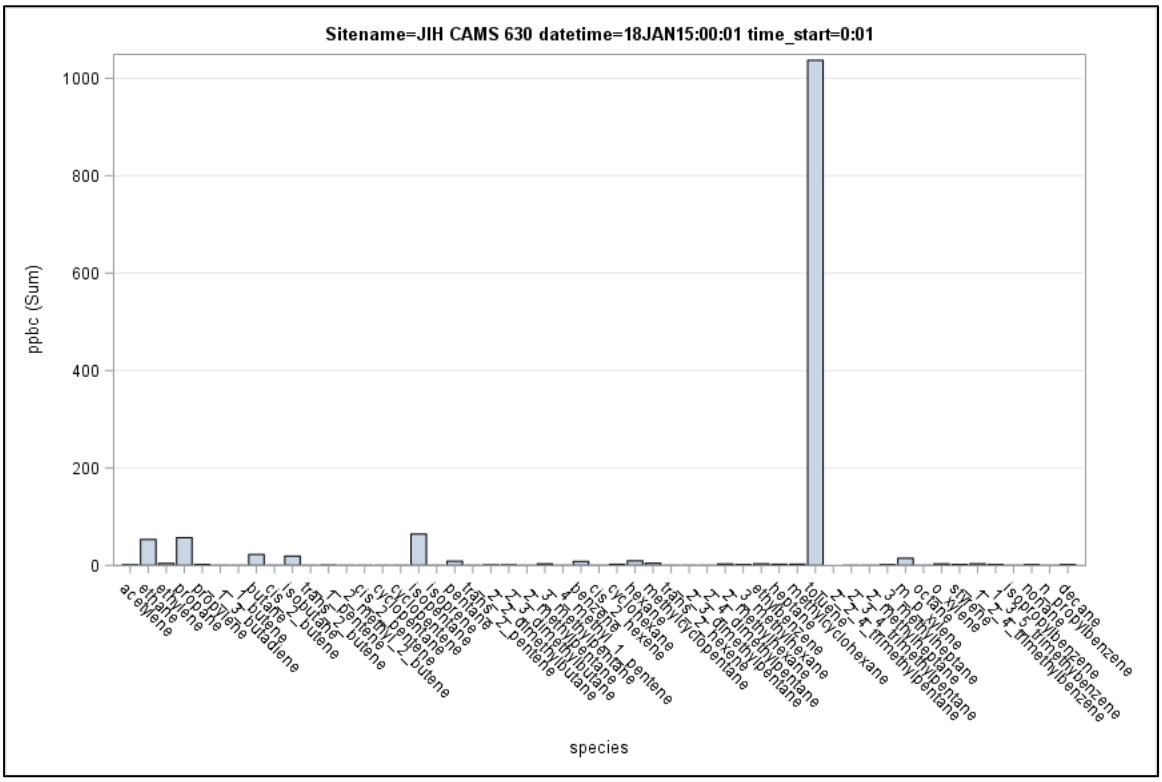


Figure 3-37. January 18 J. I. Hailey CAMS 630 canister mix of species from laboratory analysis



Case Study February 14, 2015, J. I. Hailey CAMS 630

Figure 3-38, below, shows the time series of five-minute time interval data collected at J. I. Hailey CAMS 630 overnight on February 13 – 14, 2015, for wind direction (WDR), TNMHC, methane, and canister pressure and mass flow. The graph has an arrow and label indicating when the canister sample was taken. The graph shows that TNMHC concentrations rose rapidly around 1:20 CST on February 14 with winds from the south-southwest. After sustained elevated concentrations had been measured, a canister was triggered at 1:38 CST. Figure 3-39, page 3-34, shows a surface back-trajectory begun at JIH at 1:30 CST and extending back to the south. The back trajectory suggests that the air reaching the site had passed over docks and the industrial area south across the ship channel. There was no coincident change in methane concentrations. Figure 3-40, page 3-34, shows the mix of species from the canister analysis. The large majority of material in the canister was in the two butane and two pentane species, with a notable absence of ethane and propane. This was likely some petroleum product. No values exceeded AMCVs.

Figure 3-38. February 13 – 14, 2015, J. I. Hailey CAMS 630 five-minute time interval data

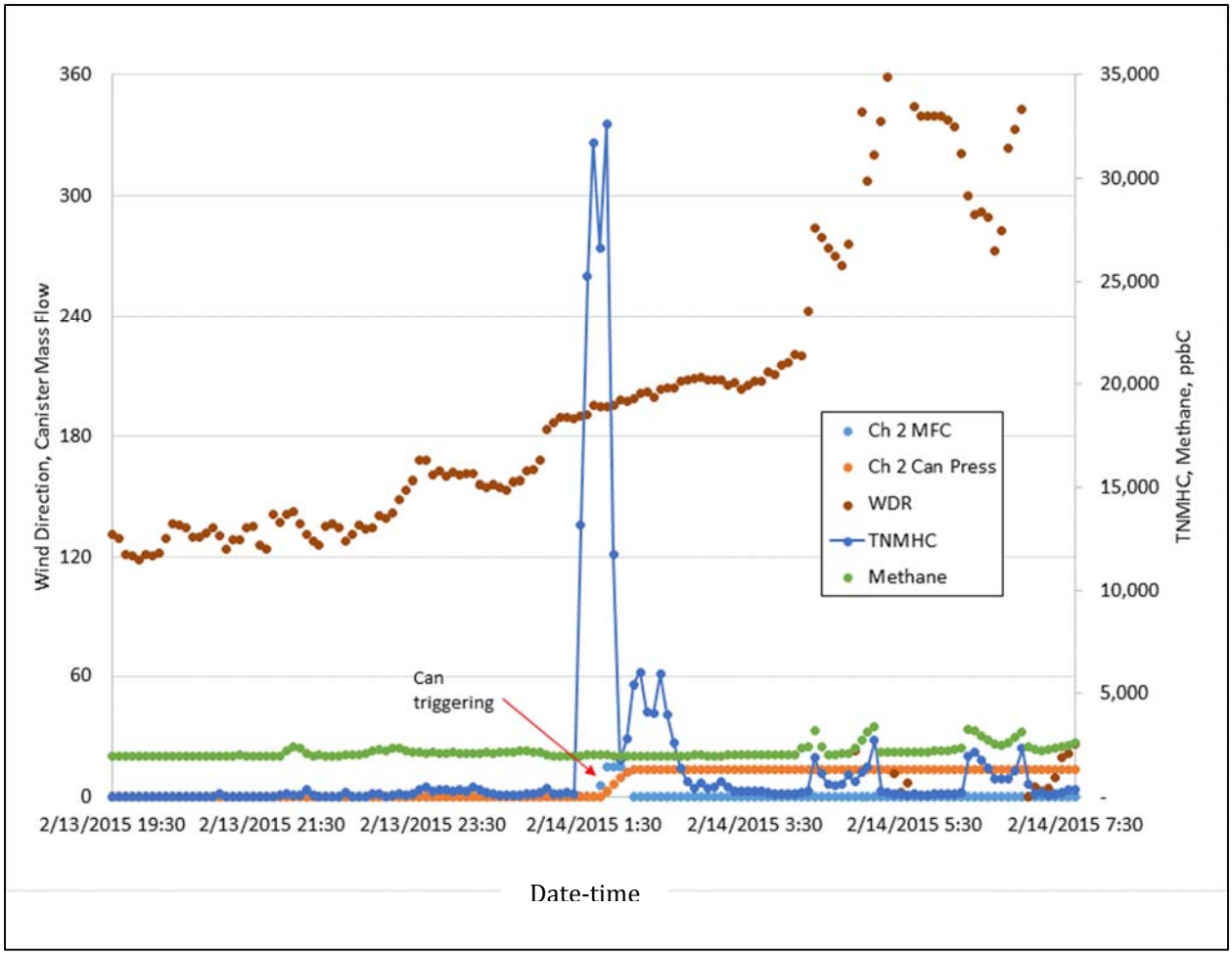


Figure 3-39. February 14, 2015, J. I. Hailey CAMS 630 surface back-trajectory begun at 1:30 CST and extending south

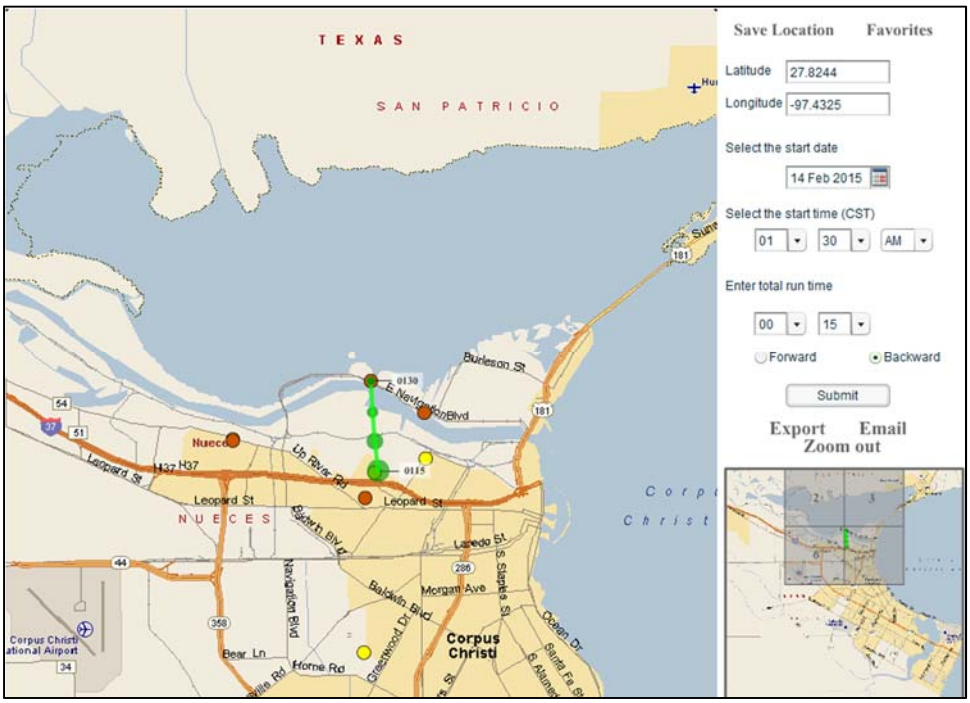
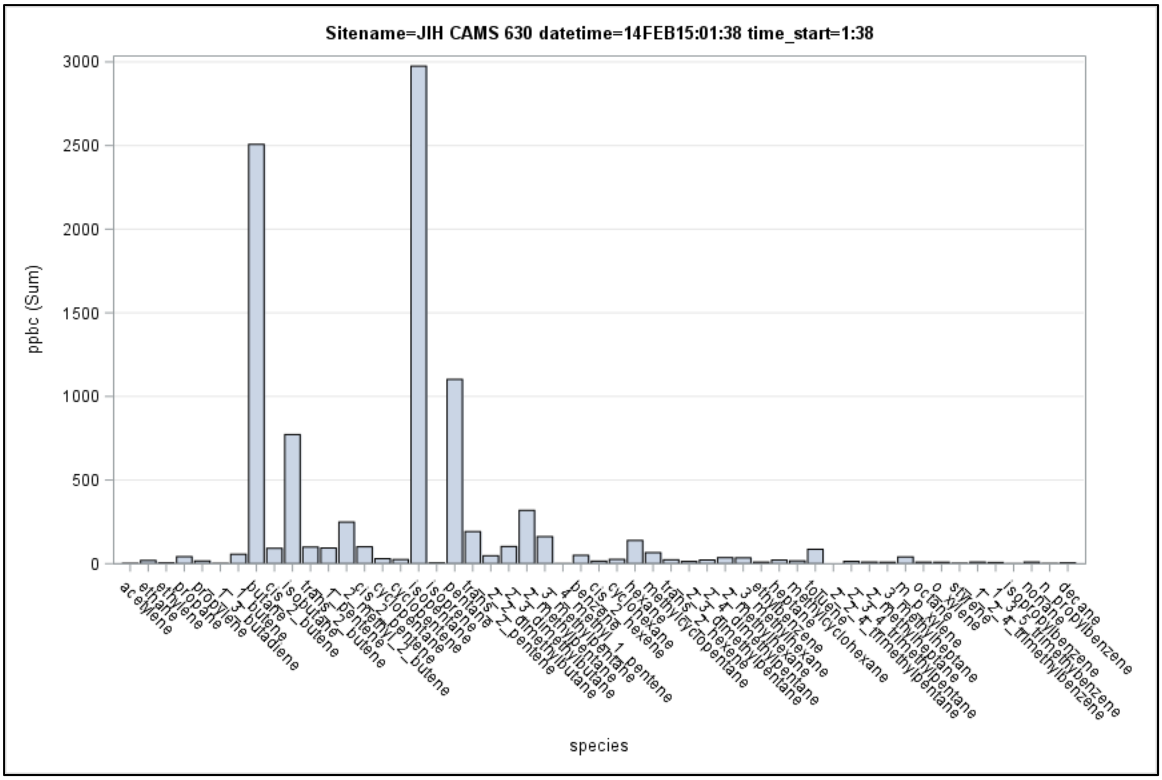


Figure 3-40. February 14, 2015, J. I. Hailey CAMS 630 canister species from laboratory analysis



3.5.3 West End Inner Harbor CAMS 631

West End Inner Harbor CAMS 631 Site Characteristics

The West End Inner Harbor CAMS 631 site was located at 3149B Suntide Road, Corpus Christi, TX 78402, at latitude 27º 50' 43" North (27.8453º), longitude -97º 31' 32" West (-97.5256º), and elevation 12.0 m. The site was recorded with the EPA site number 483550038, and TCEQ CAMS number 631. It was activated on November 29, 2004, and began producing data in mid-December. The site was decommissioned on May 15, 2012. Unlike the other six monitoring sites in this project, this site's operations ended in 2012 owing to roadway expansion. Some effort was made to find a replacement site, but the ultimate decision was to put the shelter and monitoring equipment in storage for spares and conserve resources to extend in time the operations of the other sites.

An aerial image of the site appears in Figure 3-41, below. The site was located just off the Fulton Turnpike, with exposure to the southeast to docks and to the south to the FHR Refinery, and with exposure to the Nueces Bay to the north. Figure 3-42, page 3-36, shows a higher altitude aerial image of the site relative to the ship channel, roads, industrial facilities, and the Nueces Bay.

The site was generally unobstructed with regard to wind flow from the north through west to south; however, occasionally there would be piles of road-building material nearby that may have frequently compromised wind directions from the east. Figure 3-43, page 3-36, shows a histogram of the wind directions measured over 11.5 years at FHR, and Figure 3-44, page 3-37, shows the histogram of the wind speeds.

Figure 3-41. West End Inner Harbor CAMS 631 aerial view (Dec. 2009)

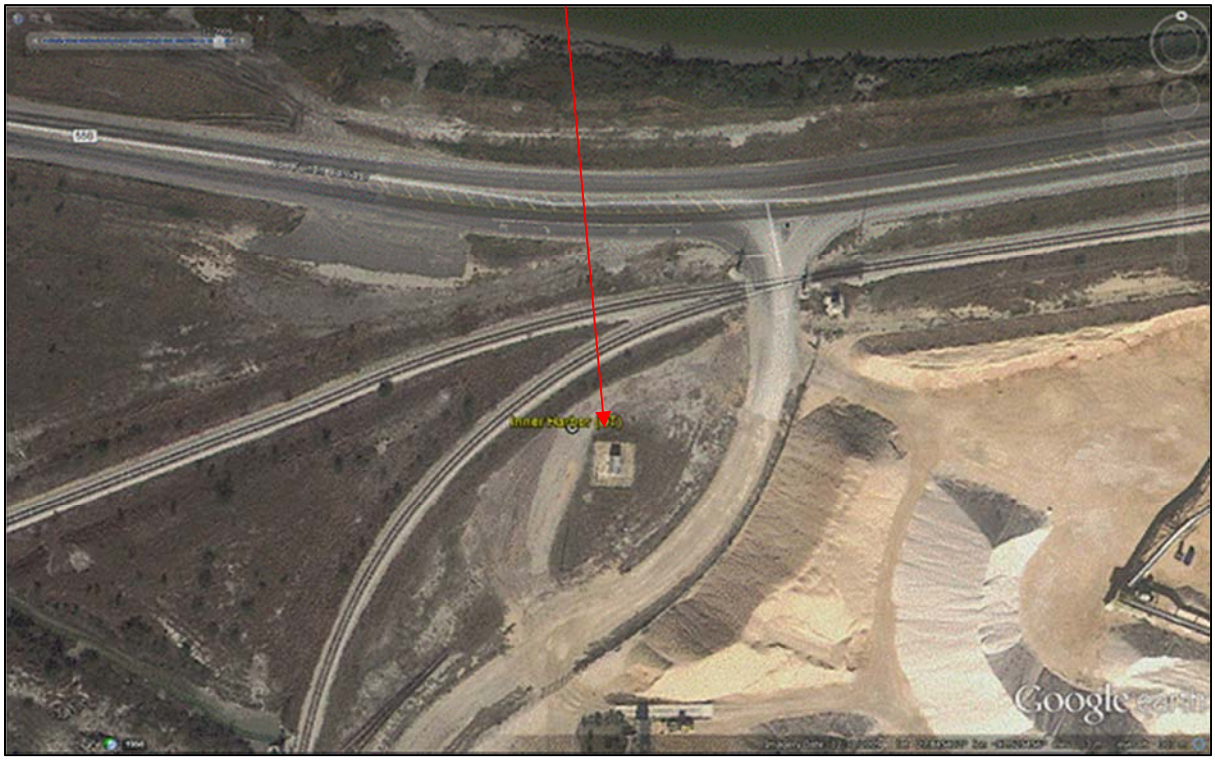


Figure 3-42. West End Inner Harbor CAMS 631 site aerial view

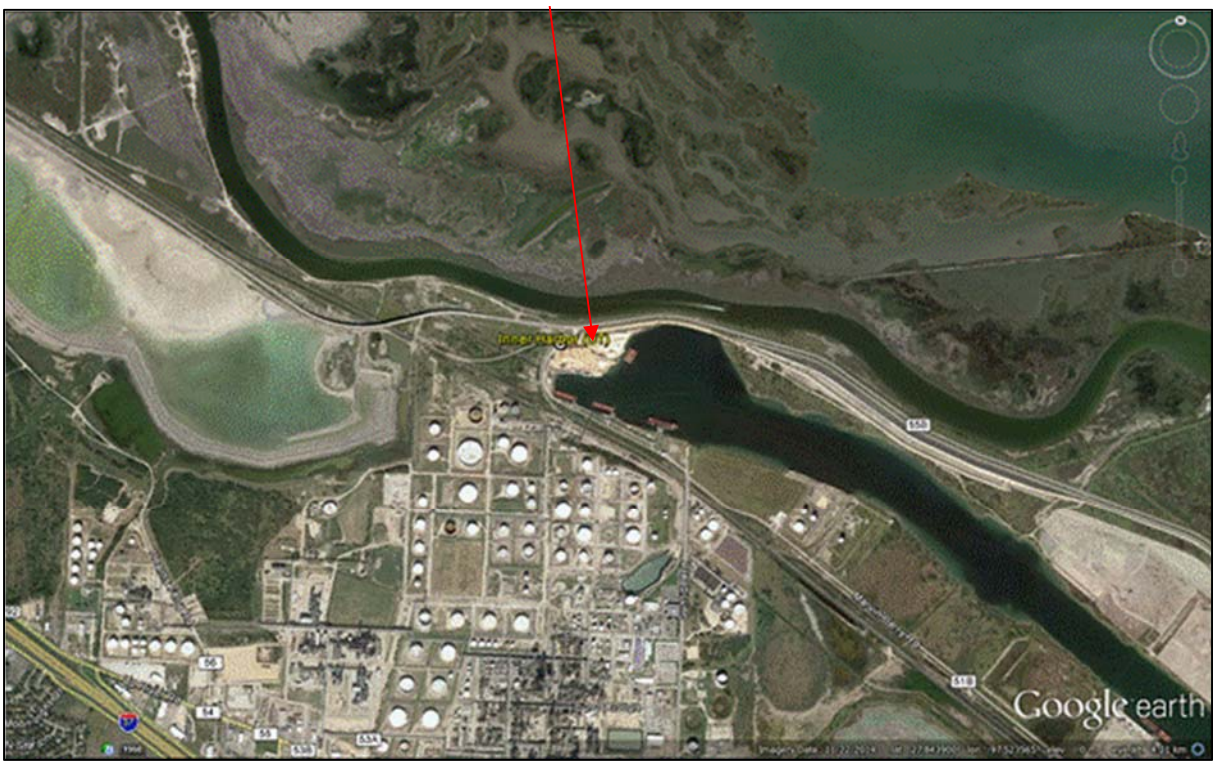


Figure 3-43. West End Inner Harbor CAMS 631 wind direction distribution

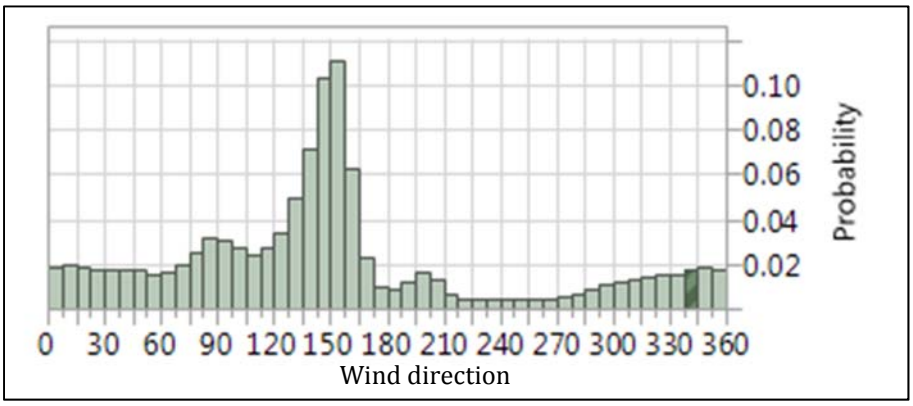
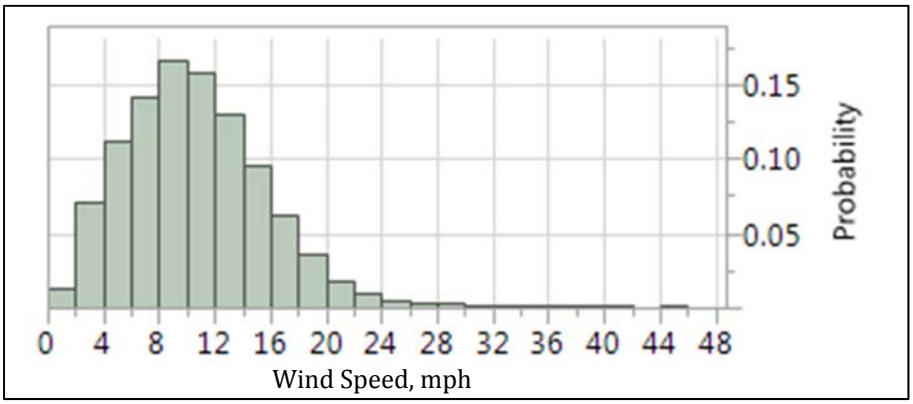


Figure 3-44. West End Inner Harbor CAMS 631 wind speed distribution



West End Inner Harbor CAMS 631 TNMHC

Figure 3-45, page 3-38, shows the time series for hourly TNMHC measurements from the West End Inner Harbor site. In the first years of operating the site, TNMHC concentrations were cropped at 10,000 ppbC. After the cropping was lifted, one hourly concentration over 10,000 ppbC was measured at the site, that being 30,223 ppbC on Feb. 24, 2009, at 19 CST under 17 mph southerly winds.

Figure 3-46, page 3-38, shows the time series for the mean TNMHC concentration by quarter of the year. There was a statistically significant decline in TNMHC mean quarterly concentrations through the end of operations at the site.

Figure 3-47, page 3-39, is a CPF contour plot of the frequency with which a TNMHC concentration exceeds the 95th percentile 5-minute value of 561 ppbC over the period of monitoring. The image is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows that the upper 5-percentile highest concentrations came from south southeast, and the frequency declined but was still the strongest direction of elevated concentrations up until the site decommissioning.

Figure 3-45. Time series for hourly TNMHC concentrations, ppbC units, West End Inner Harbor CAMS 631 site

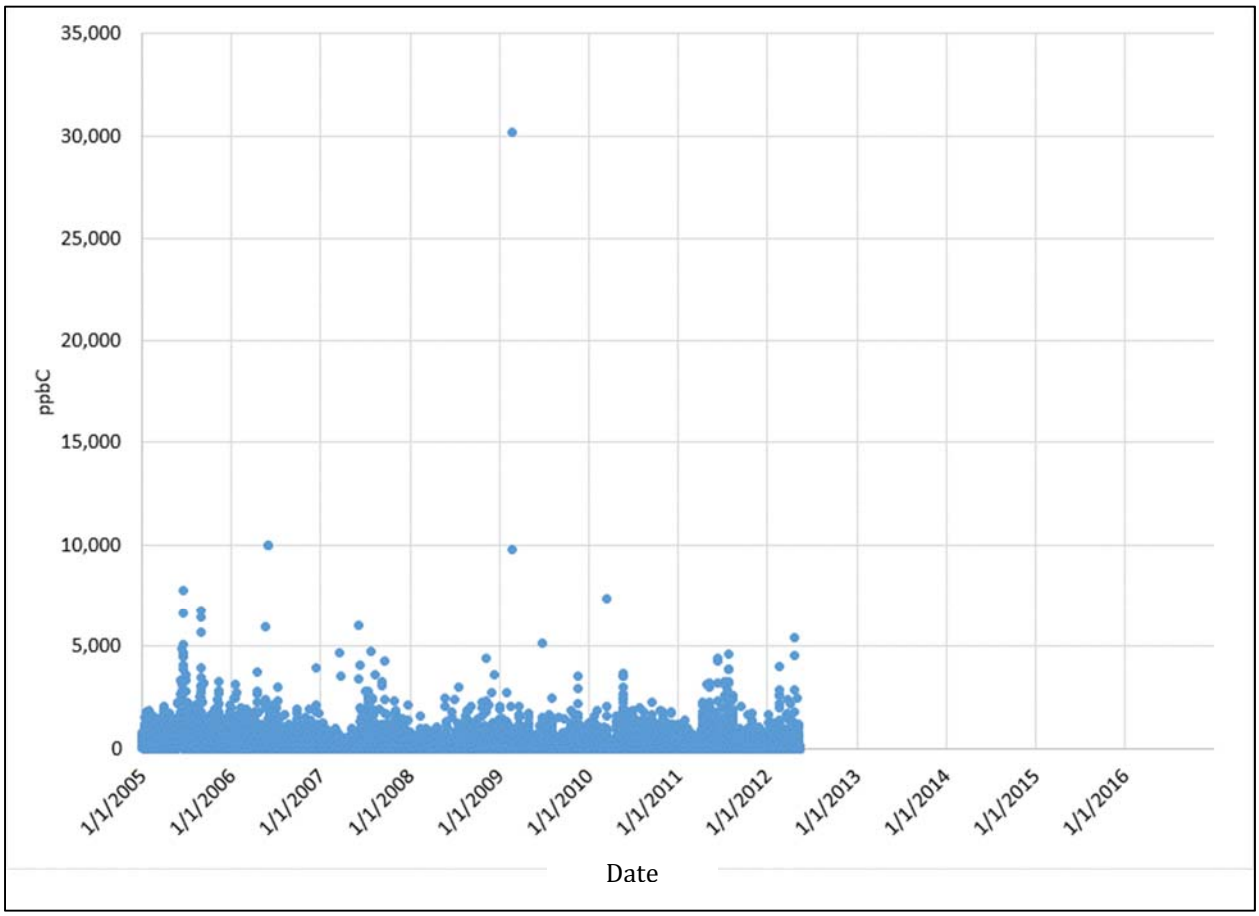


Figure 3-46. West End Inner Harbor CAMS 631 TNMHC quarterly mean concentrations, Jan. 2005 – May 2016

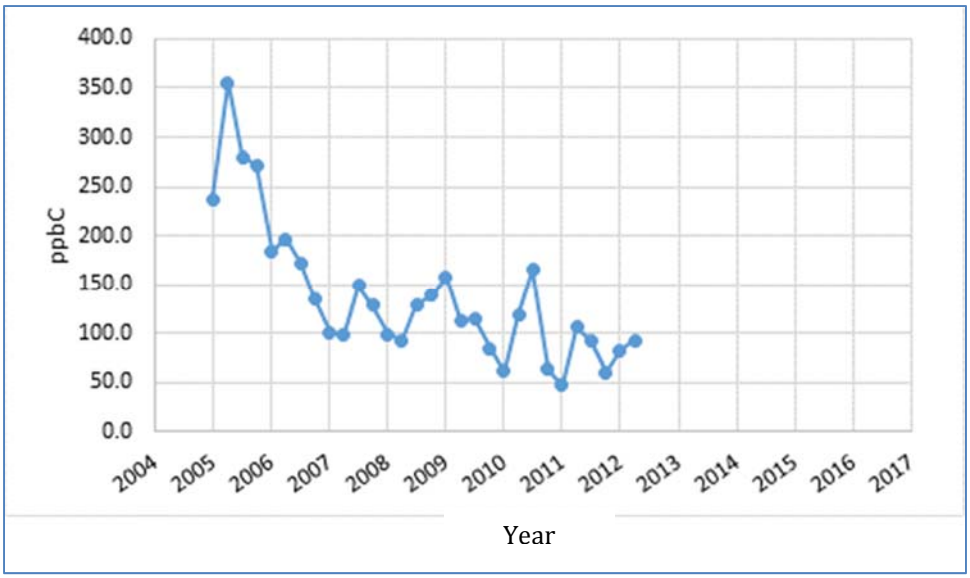
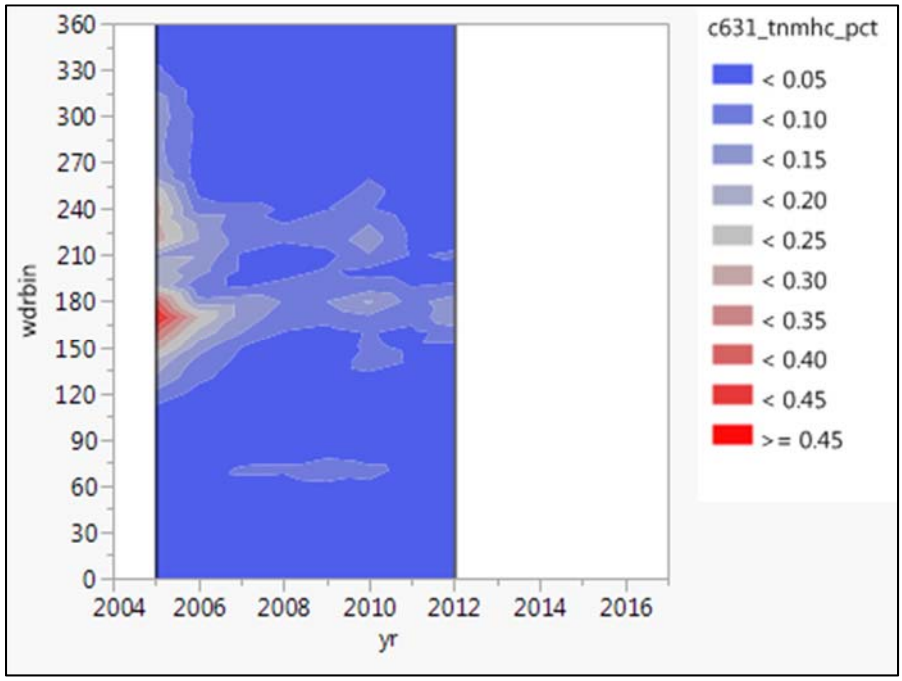


Figure 3-47. Contour plot of frequency that TNMHC concentrations exceeded the 95th percentile 5-minute value for TNMHC at West End Inner Harbor CAMS 631



West End Inner Harbor CAMS 631 SO_2

At West End Inner Harbor, the SO_2 concentrations declined faster than at the other sites, getting down close to 0.0 ppb mean concentration by 2012. Figure 3-48, page 3-40, shows the time series for hourly SO_2 measurements. There was a clearly a decrease in the frequency of elevated concentrations over time. Figure 3-49, page 3-40, shows a graph of the mean SO_2 concentration by quarter of the year.

Figure 3-50, page 3-41, is a CPF contour plot of the frequency with which an SO_2 concentration exceeded the 95th percentile 5-minute value of 1.1 ppb over the period of monitoring. The image in Figure 3-50 is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows that up until 2008, the highest concentrations came from the southeast direction, pointing back to the dock area. Over the last few years, the frequency of upper 5 percentile values significantly declined.

Figure 3-48. West End Inner Harbor **CAMS 631 SO_2 time series, Jan. 2005 – May 2012**

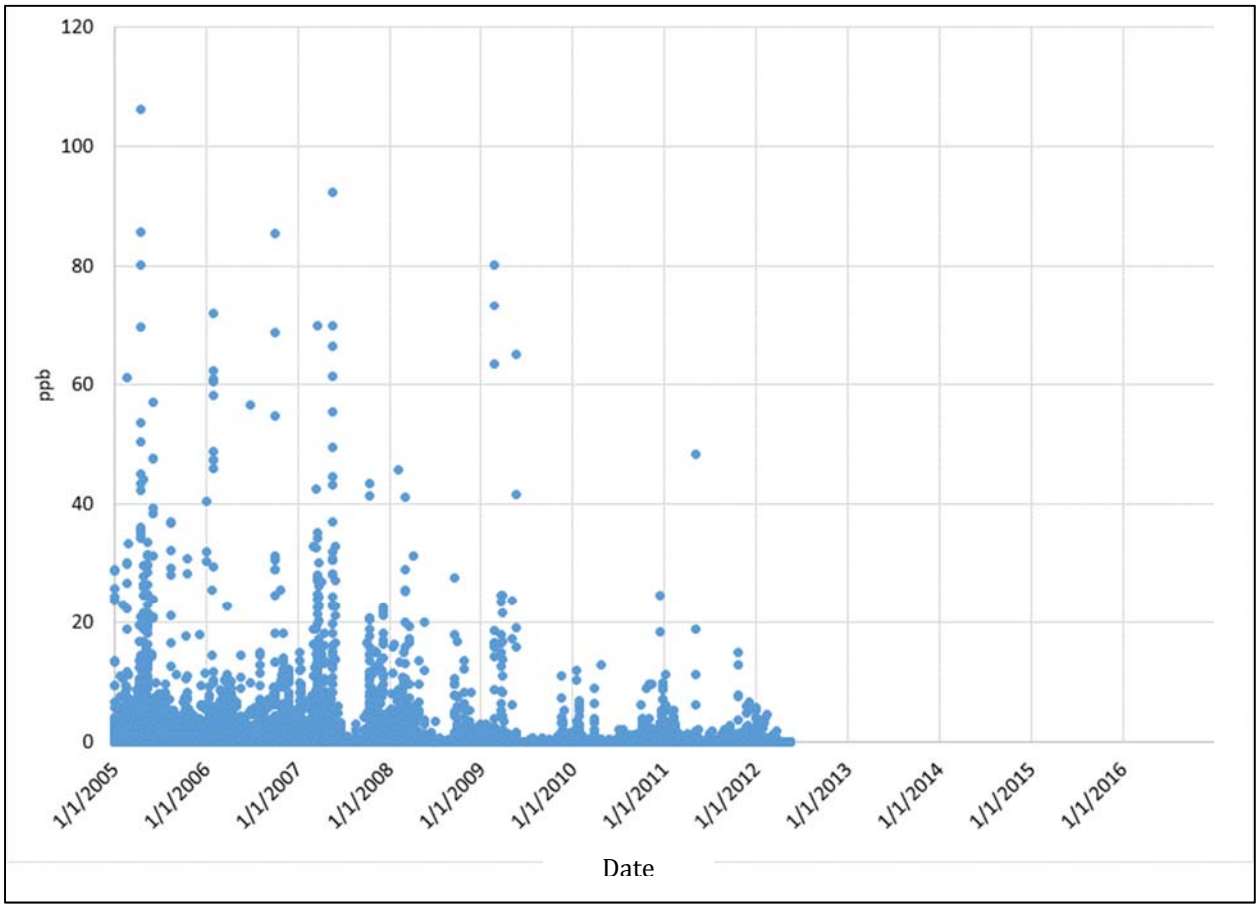


Figure 3-49. West End Inner Harbor CAMS 631 SO_2 quarterly mean concentrations, Jan. 2005 – May 2016

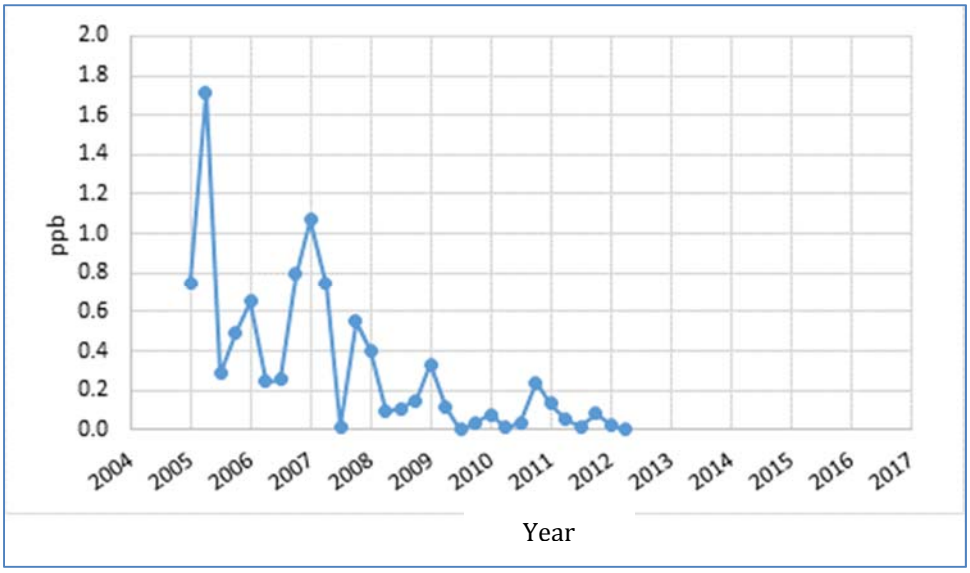
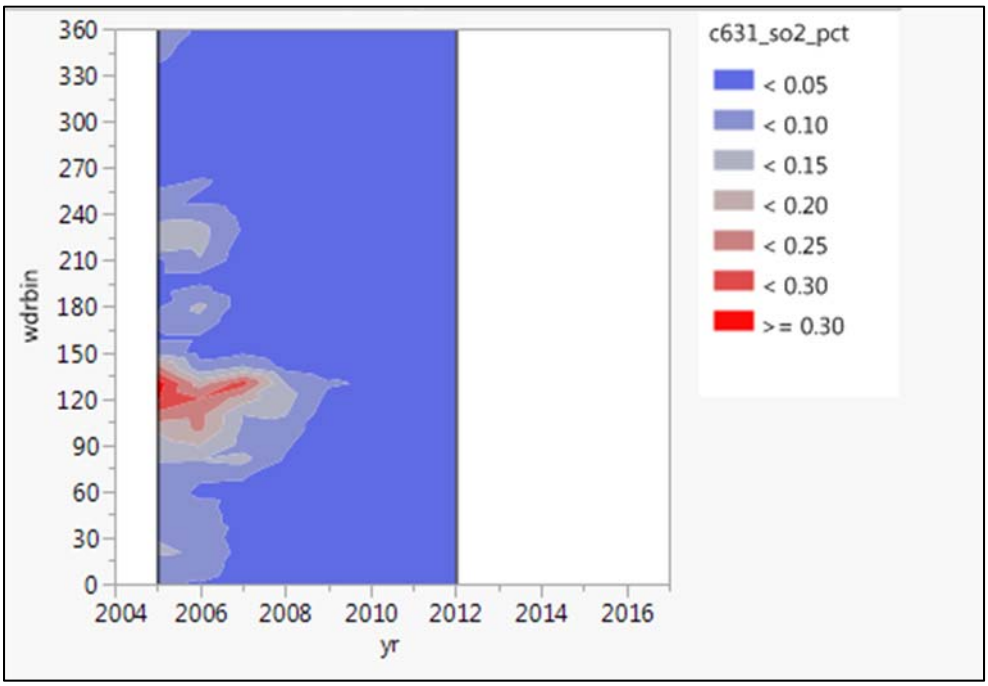


Figure 3-50. Contour plot of frequency that SO_2 concentrations exceeded the 95th percentile 5-minute value for SO_2 at West End Inner Harbor CAMS 631



West End Inner Harbor CAMS 631 H_2S

The third pollutant measured at the West End Inner Harbor site was hydrogen sulfide (H_2S). Concentrations of this pollutant declined to the near 0.0 background conditions by early 2012. Figure 3-51, page 3-42, shows the time series for hourly H_2S measurements. The highest single one-hour observation of 77 ppb was taken on January 19, 2005, at 21 CST. During this episode, the TCEQ's 30-minute 80-ppb H_2S standard was violated with a 30-minute maximum of 85 ppb. Figure 3-52, page 3-42, shows a graph of the mean H_2S concentration by quarter of the year. The CPF contour plot in Figure 3-53, page 3-43, shows the wind directions and time periods that H_2S concentration exceeded the 95th percentile 5-minute value of 2.3 ppb, which were measured around 210 degrees up until 2011.

Figure 3-51. West End Inner Harbor CAMS 631 H_2S time series, Jan. 2005 – May 2012

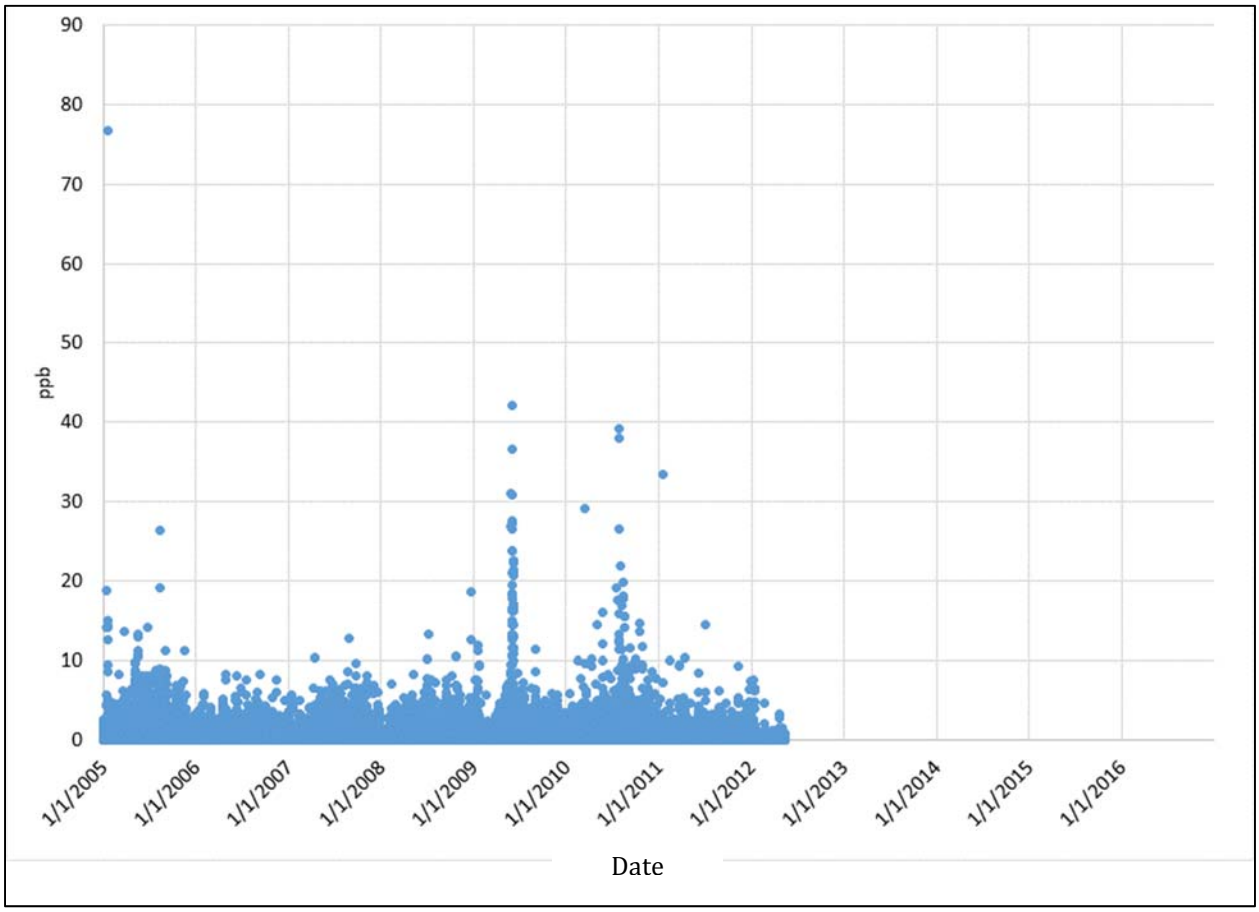


Figure 3-52. West End Inner Harbor CAMS 631 H_2S quarterly mean concentrations, Jan. 2005 – May 2016

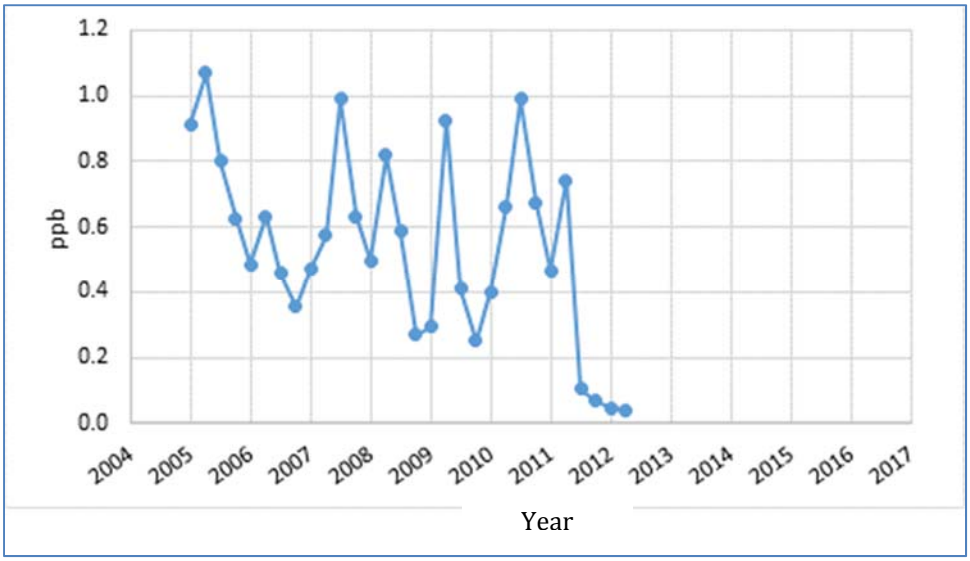
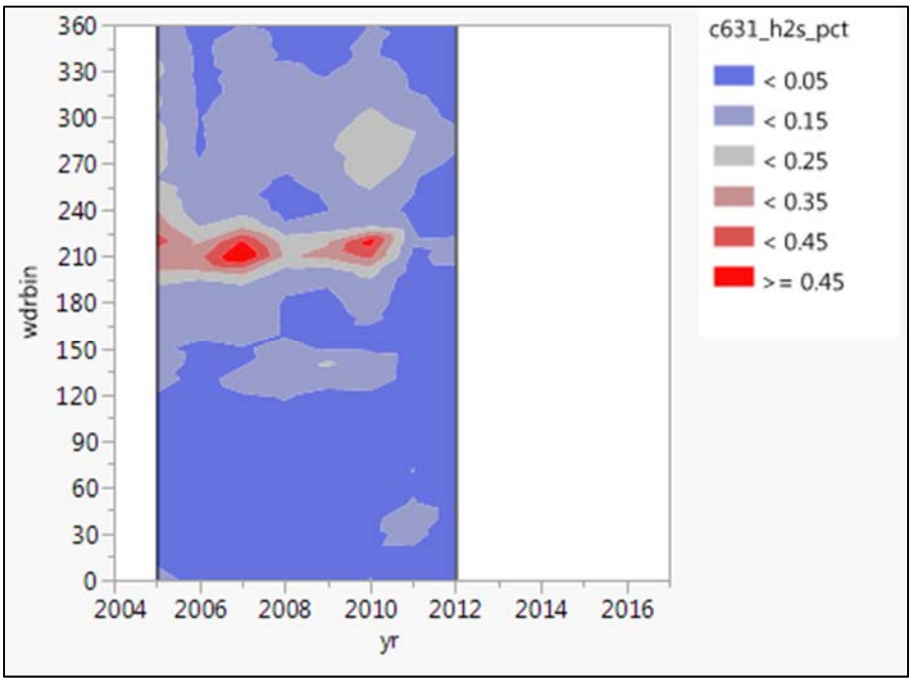


Figure 3-53. Contour plot of frequency that H_2S concentrations exceeded the 95th percentile 5-minute value for H_2S at West End Inner Harbor CAMS 631



Case Study: New emission source found

Several email alerts were generated in March 2012 on TNMHC concentrations above 2000 ppbC under northerly winds at the West End Inner Harbor site. Few if any alerts of this nature had been received prior to this. Coincident with the elevated TNMHC were elevated methane levels. A time-series graph of 5-minute methane values for 2012 is shown in Figure 3-54, page 3-44. In order to assess the behavior of methane concentrations at West End Inner Harbor, the measurements from the month of March for each year were examined. Figure 3-55, on page 3-45, is a collection of graphs of methane by wind direction at 5-minute time scale for months of March from 2005 – 2012. Only in 2012 and only from northeast winds were levels over 5000 ppbC measured. Coincident TNMHC and methane concentration generally means natural gas has been emitted upwind. Figures 3-56 and 3-57, on page 3-46, show the mean methane and mean TNMHC by wind direction, respectively for March 2012. Both graphs show the same direction peak at 30 degrees. This direction was placed on an aerial map, and an exposed gas pipeline service outlet was identified 130 meters away from the site in the key upwind direction. UT Austin contacted the contractor for site operations on April 6, 2012, to ask if any unusual activity could be observed northeast of the site. The contractor responded that one operator stated "I can hear the gas blowing out the top clamp on the top of the riser. I notified Enterprise (the pipeline owner)." A second operator's response was: "I heard it the other day when I was doing LCCs. May be coming out of the pressure release valve." A photo of the service outlet appears in Figure 3-58, on page 3-47. The elevated methane and TNMHC were not observed after the pipeline operator was notified.

Figure 3-54. Methane five-minute ppbC concentrations increased in March 2012

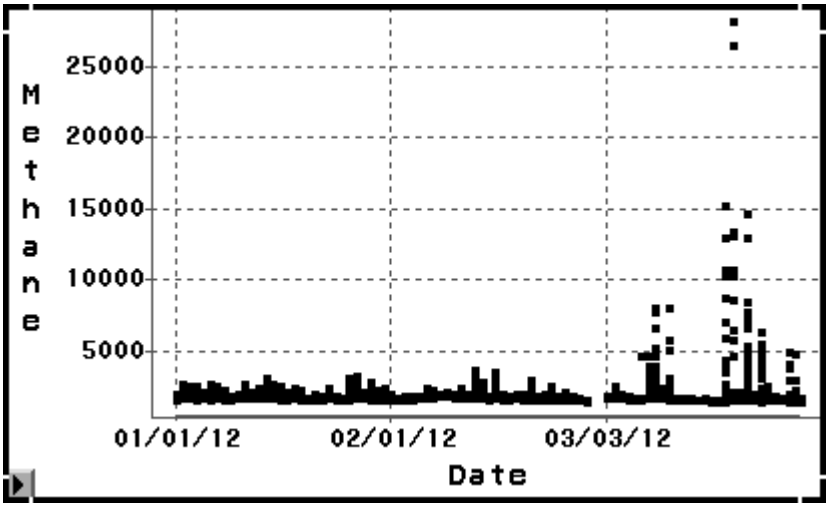


Figure 3-55. Methane vs. wind direction at 5-minute time scale for the month of *March* by year

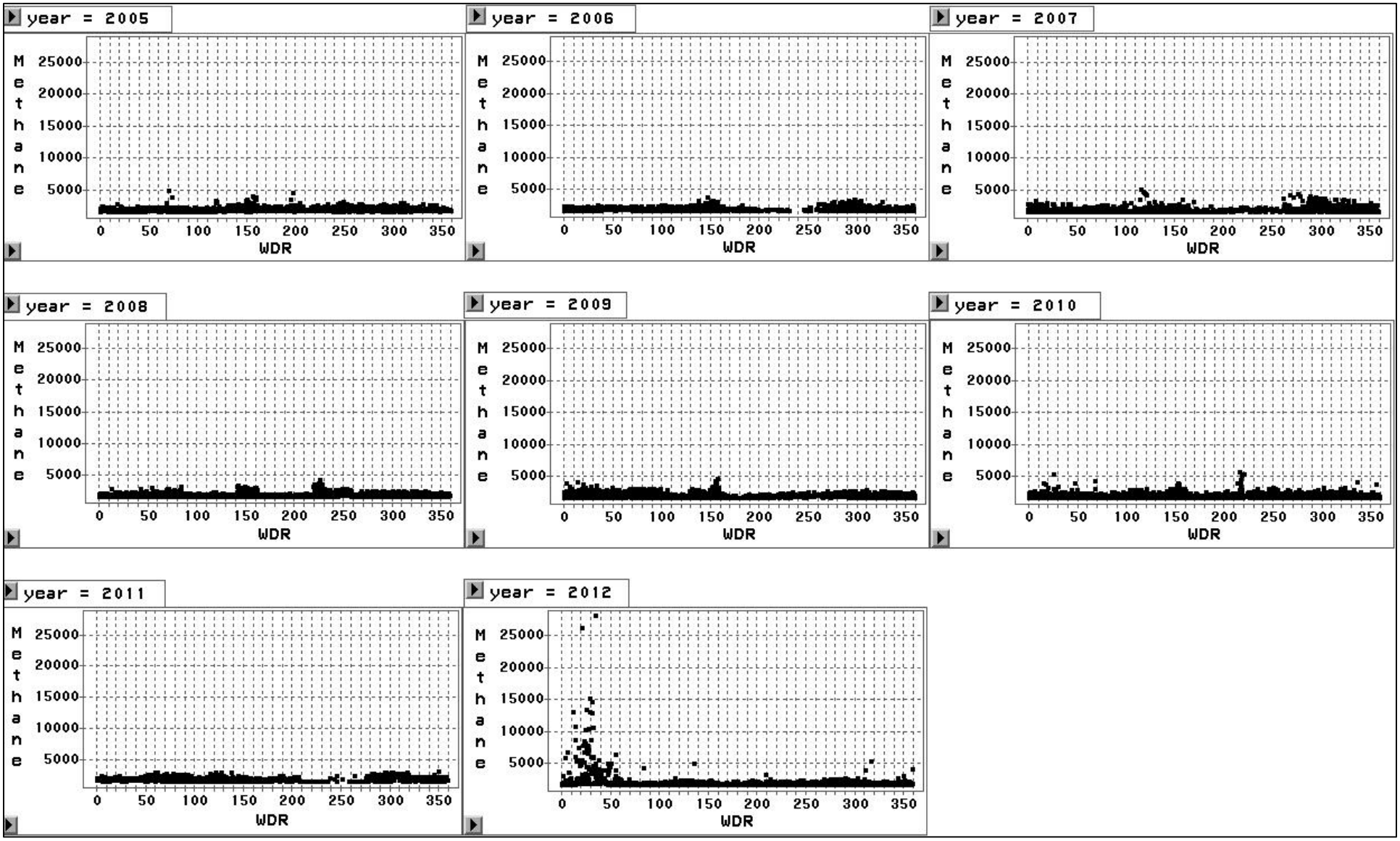


Figure 3-56. Mean ppb methane by wind direction, March 2012, West End Inner Harbor

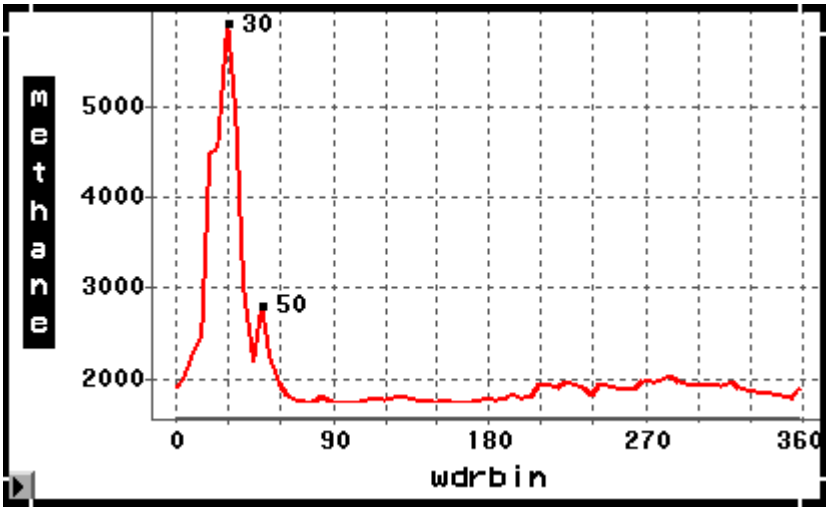


Figure 3-57. Mean ppbC TNMHC by wind direction, March 2012, West End Inner Harbor

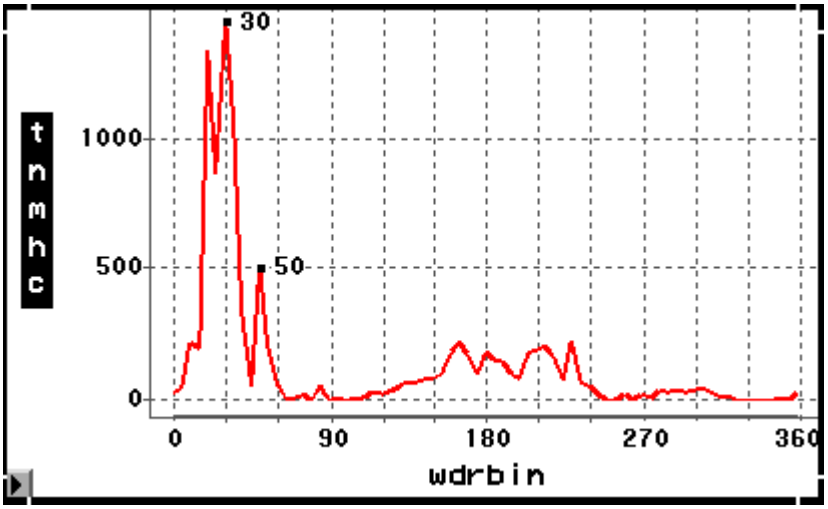


Figure 3-58. Enterprise pipeline service outlet believed to have been the source of elevated methane and TNMHC in March 2012.

3.5.4 FHR Easement CAMS 632

FHR Easement CAMS 632 Site Characteristics

The Flint Hills Resources (FHR) Easement site was located at 8401B Up River Road, Corpus Christi, TX 78409, at latitude 27º 49' 38" North (27.8272º), longitude -97º 31' 44" West (-97.5289 º), and elevation 12.0 m. The site was recorded with the EPA site number 483550039, and TCEQ CAMS number 632. It was activated on November 29, 2004, and began producing data in mid-December. The site was decommissioned on May 22, 2016. An aerial image of the site appears in Figure 3-59, below. The site was located just south of Up River Rd, surrounded by light industrial businesses and south of the FHR Refinery. Figure 3-60, page 3-49, shows a higher altitude aerial image with FHR Easement site along with nearby sites Solar Estates CAMS 633, West End Inner Harbor CAMS 631, and TCEQ Tuloso CAMS 21.

Earlier in this report on page 3-3, Table 3-2 showed the mean wind speed at FHR was 9.2 mph, suggesting fairly good exposure. Figure 3-61, page 3-49, shows a histogram of the wind directions measured over 11.5 years at FHR, and Figure 3-62, page 3-50, shows a histogram of the wind speeds.

Figure 3-59. Flint Hills Resources Easement, CAMS 632 aerial view

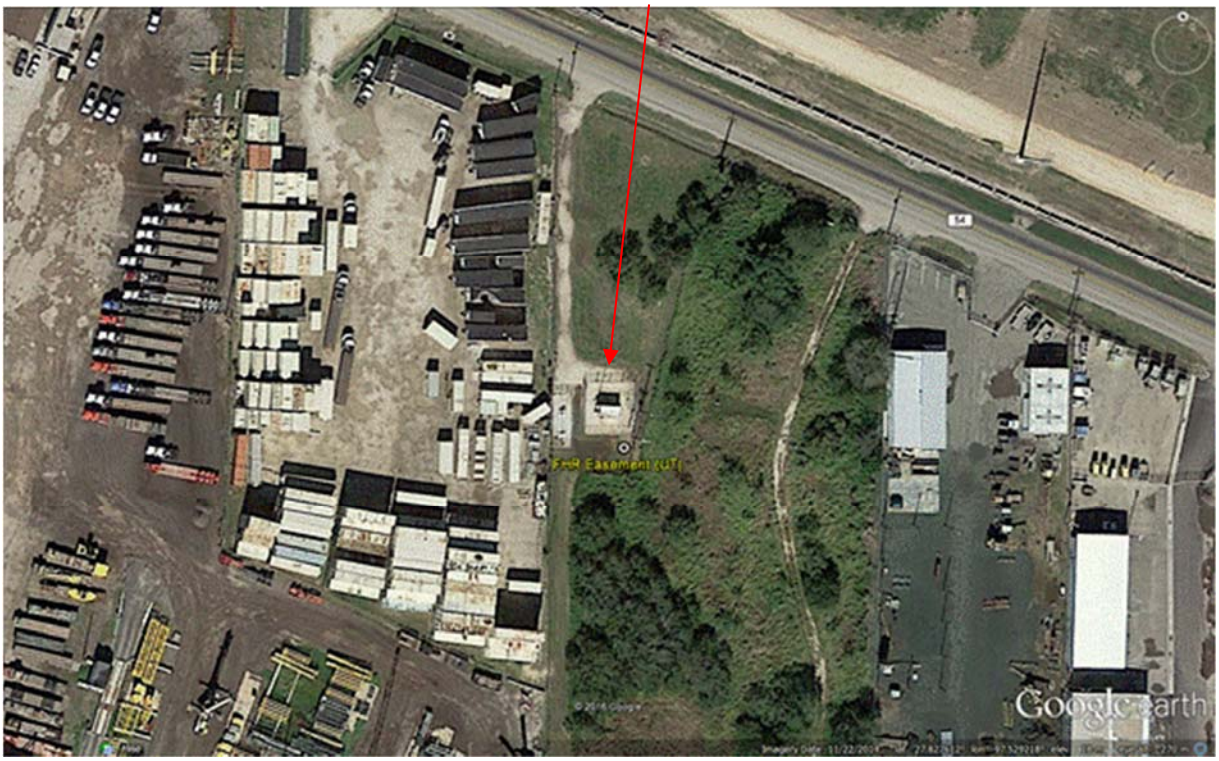


Figure 3-60. Solar Estates, FHR Ease., West End / Inner Harbor, TCEQ Tuloso aerial view from 4km

Figure 3-61. FHR Easement CAMS 632 wind direction distribution

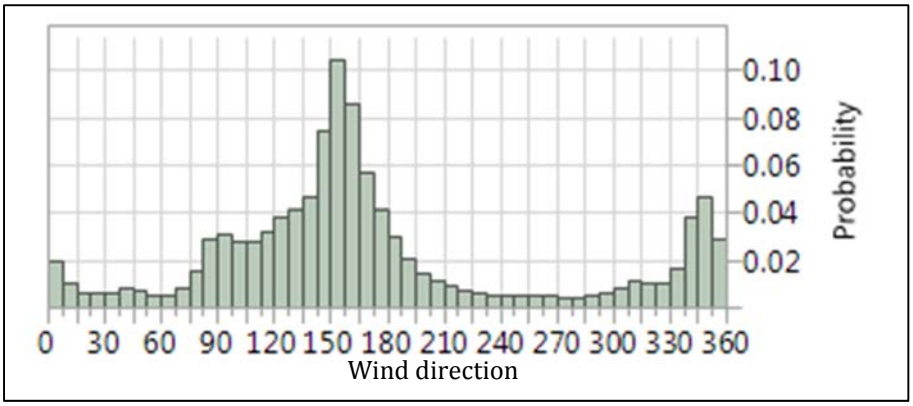
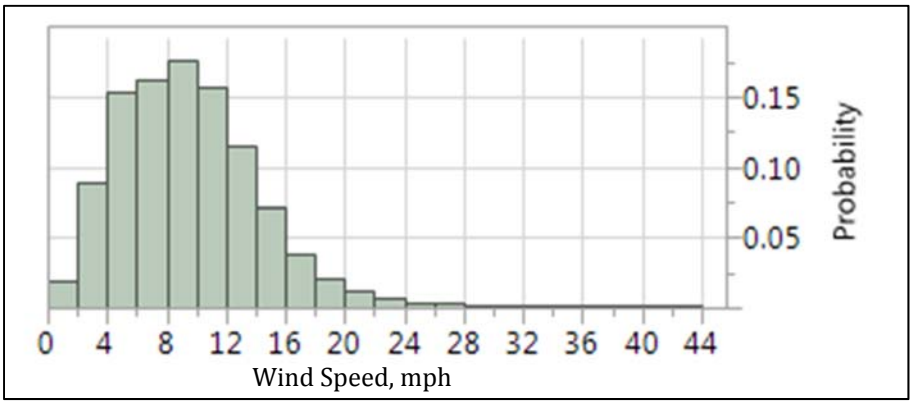


Figure 3-62. FHR Easement CAMS 632 wind speed distribution



FHR Easement CAMS 632 TNMHC

Figure 3-63, page 3-51, shows the time series for hourly TNMHC measurements from the Flint Hills site. There was a clear decline in the measurement of values above 5,000 ppbC after the first three years of operation. Two hourly values in 2006 were cropped at 10,000 ppbC. Figure 3-64, page 3-51, shows the time series for the mean TNMHC concentration by quarter of the year. After progressive declines during the first three years, concentrations appear to flatten out with a seasonal pattern persisting up until decommissioning in 2016.

Figure 3-65, page 3-52, is a CPF contour plot of the frequency with which a TNMHC concentration exceeds the 95th percentile 5-minute value over the period of monitoring. The image is color-coded for the highest frequency of exceedances of the 95th percentile 5-minute value of 793 ppbC. The figure shows that in the site's early years, the highest concentrations came from the south. The legend in the figure shows that more than 50 to 60 percent of the time that the wind blew from around 165 - 195 degrees, 5-minute values in the upper 5 percentile of measurements were recorded. As shown earlier in Figure 3-61, page 3-49, this was a relatively high frequency of occurrence. Field visits to the site showed that the likely emission source for the TNMHC was a small active pump jack and tank battery 500 feet away at a bearing of 165 degrees south of the monitoring site. A second tank battery stood 1,300 feet at a bearing of 188 degrees south of the monitoring site and may also have contributed to elevated concentrations at the site.

Figure 3-63. Time series for hourly TNMHC concentrations, ppbC units, FHR Easement CAMS 632 site

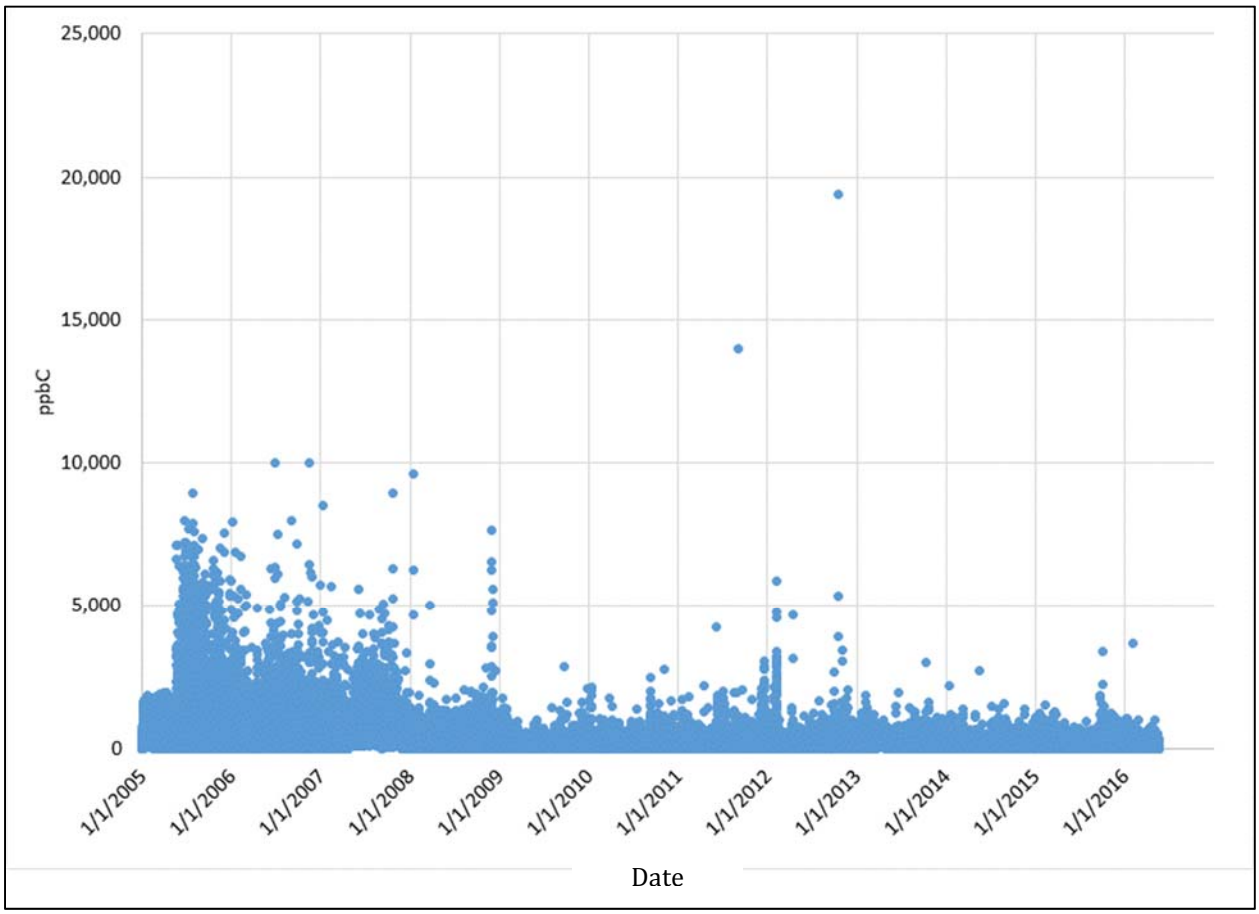


Figure 3-64. FHR Easement CAMS 632 TNMHC quarterly mean concentrations, Jan. 2005 – May 2016

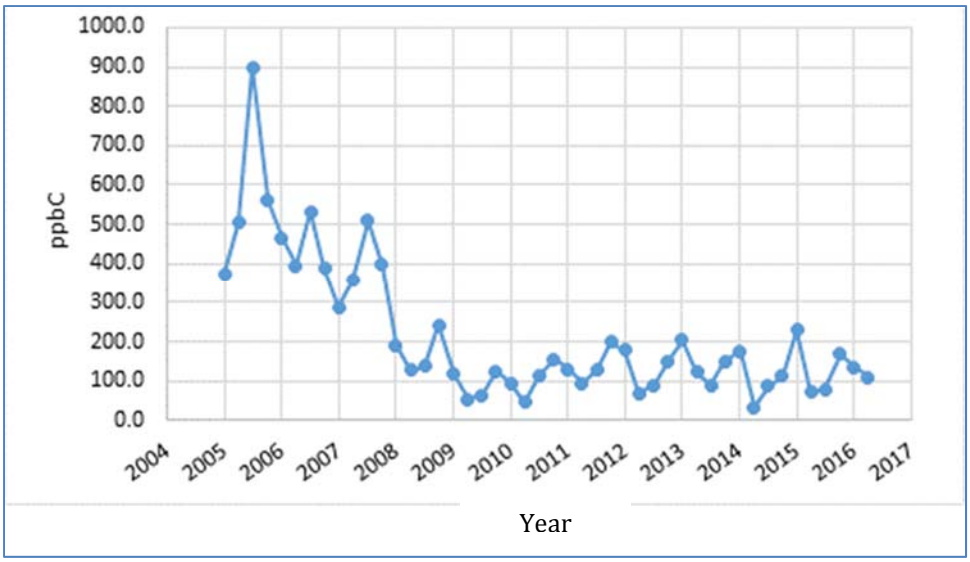
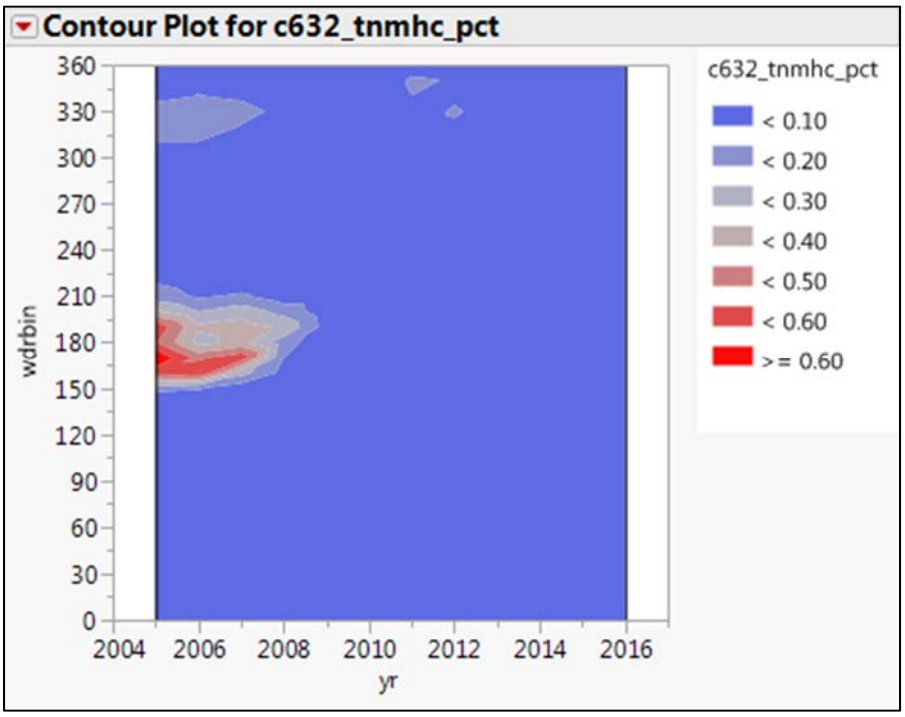


Figure 3-65. Contour plot of frequency that TNMHC concentrations exceeded the 95th percentile 5-minute value for TNMHC at FHR Easement CAMS 632



FHR Easement CAMS 632 SO_2

At FHR Easement, the SO_2 concentrations significantly declined since monitoring began. Figure 3-66, page 3-53, shows the time series for hourly SO_2 measurements. There was very clearly a decrease in the frequency of elevated concentrations over time. However, the highest SO_2 one-hour value at the site occurred relatively recently on May 14, 2014.

Figure 3-67, page 3-53, shows a graph of the mean SO_2 concentration by quarter of the year. Like other sites in recent years, the large majority of measurements in the last few quarters of site operation have been within the margin of error of 0.0 ppb, with only occasional measurements as high as 10 ppb. Thus, in Figure 68, the quarterly mean concentrations appear to bottom out close to 0.0 ppb.

Figure 3-68, page 3-54, is a CPF contour plot of the frequency with which an SO_2 concentration exceeds the 95th percentile 5-minute value over the period of monitoring. At FHR Easement, only 5 percent of all 5-minute time scale measurements were greater than 1.7 ppb. The image in Figure 3-68 is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows that the key direction for elevated SO_2 was to the northeast, between 0 and 60 degrees, which would point towards the stacks in the nearby refinery.

Figure 3-66. FHR Easement CAMS 632 Flint Hills Refinery Easement SO_2 time series, Jan. 2005 – May 2016

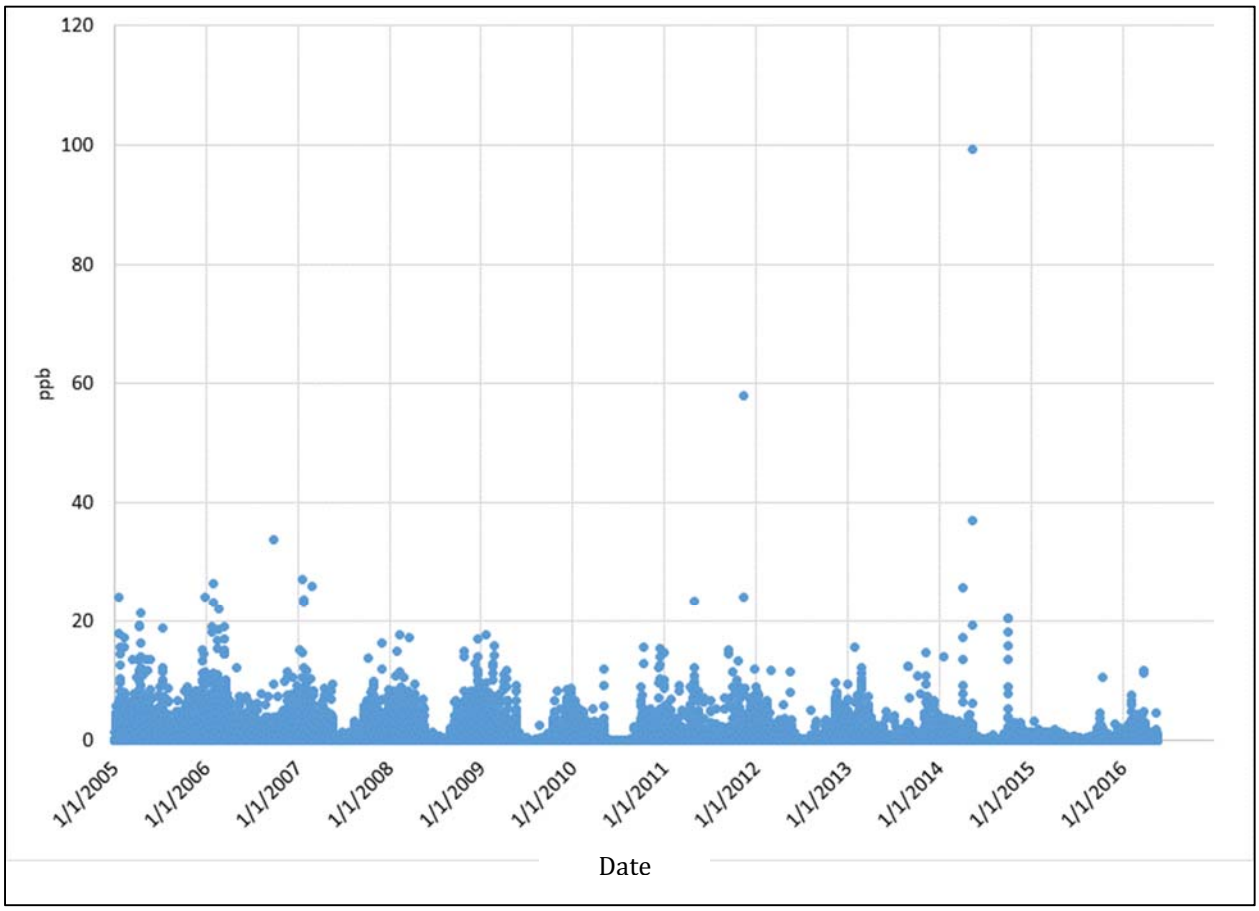


Figure 3-67. FHR Easement CAMS 632 SO_2 quarterly mean concentrations, Jan. 2005 – May 2016

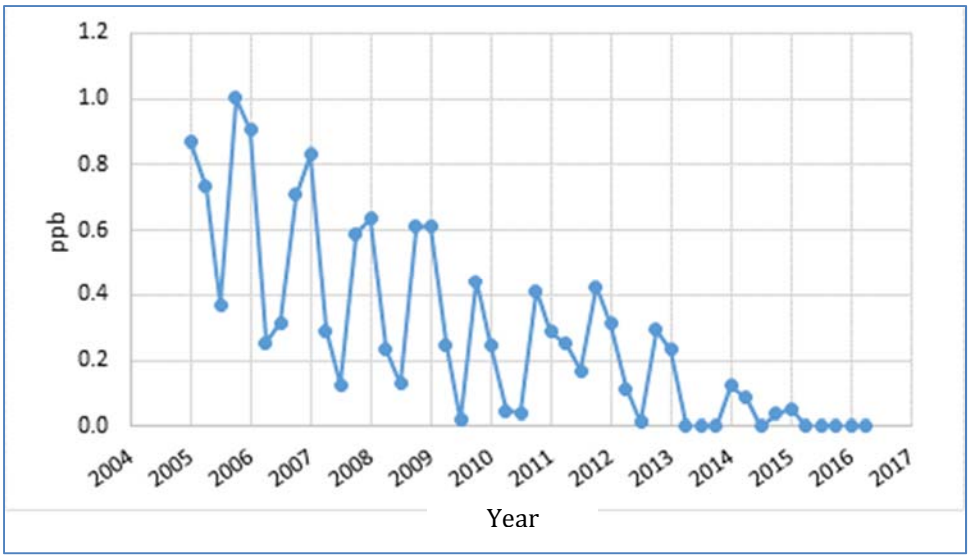
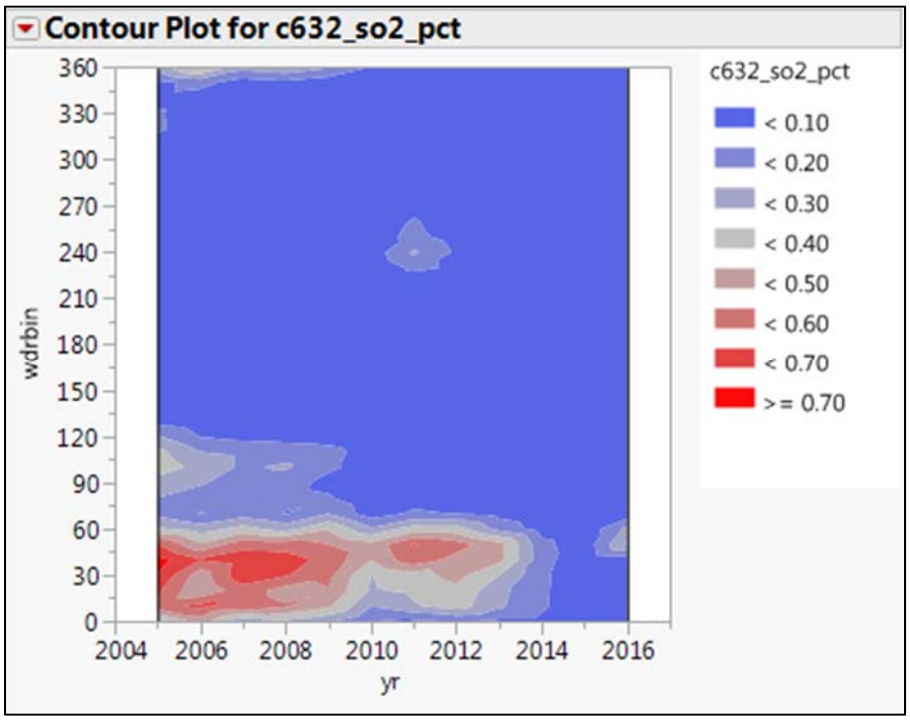


Figure 3-68. Contour plot of frequency that SO_2 concentrations exceeded the 95th percentile 5-minute value for SO_2 at FHR Easement CAMS 632



FHR Easement CAMS 632 H_2S

At FHR Easement, the H_2S concentrations have declined to some extent, but not to near-0.0 ppb levels. Figure 3-69, page 3-55, shows the time series for hourly H_2S measurements. On Sept. 4, 2011, the FHR Easement site recorded exceedances of the TCEQ's 80 ppb 30-minute H_2S standard with a peak 30-minute average concentration of 102 ppb and 5-minute peak concentration of 288 ppb.

Figure 3-70, page 3-55, shows a graph of the mean H_2S concentration by quarter of the year. The quarterly mean concentrations still show the presence of detectable levels of H_2S.

Figure 3-71, page 3-56, is a CPF contour plot of the frequency with which an H_2S concentration exceeds the 95th percentile 5-minute value over the period of monitoring. At FHR Easement, only 5 percent of all 5-minute time scale measurements were greater than 1.2 ppb. The image in Figure 3-71 is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows that the key direction for elevated H_2S was to the northeast and northwest, which would point towards the nearby refinery.

Figure 3-69. Time series for hourly H_2S concentrations, ppbC units, FHR Easement CAMS 632 site

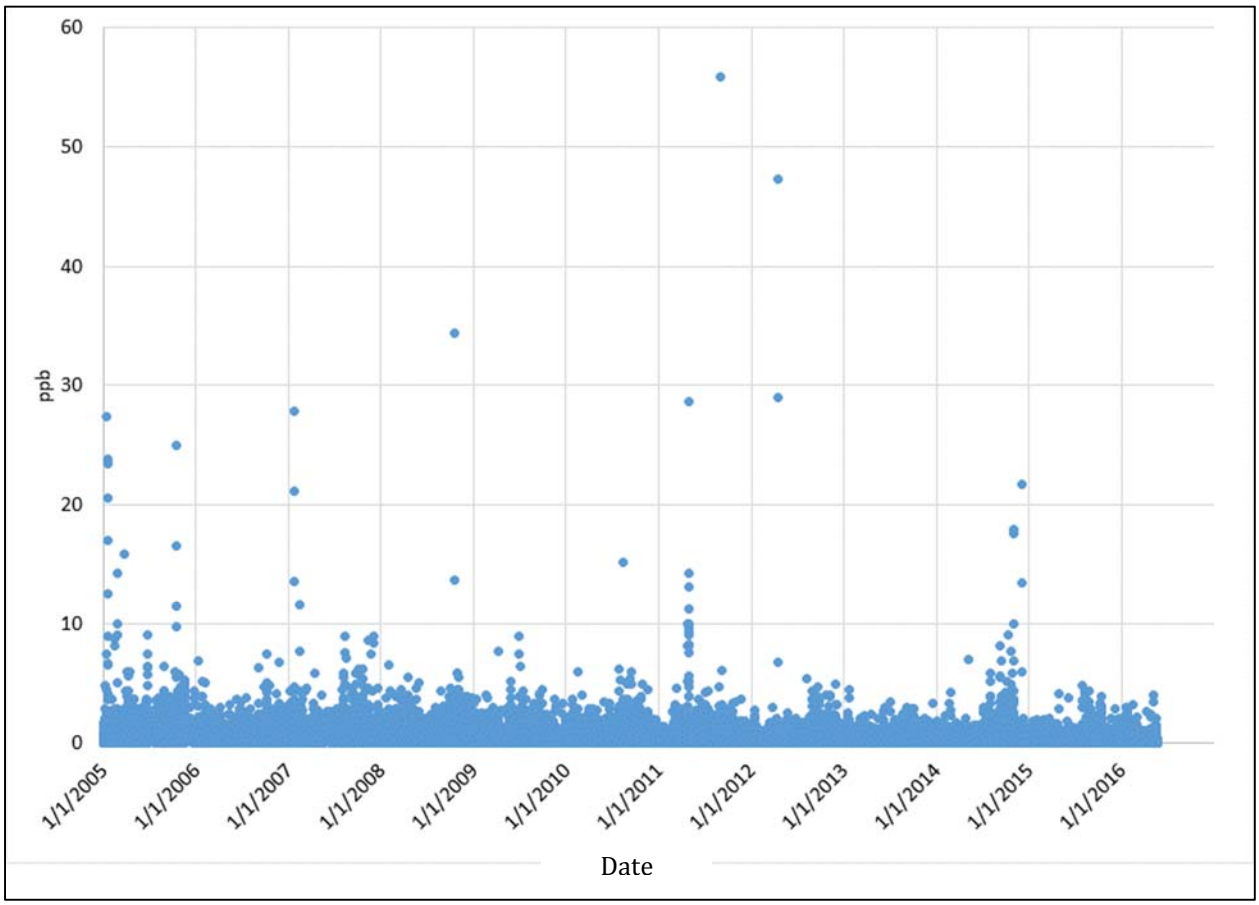


Figure 3-70. FHR Easement CAMS 632 H_2S quarterly mean concentrations, Jan. 2005 – May 2016

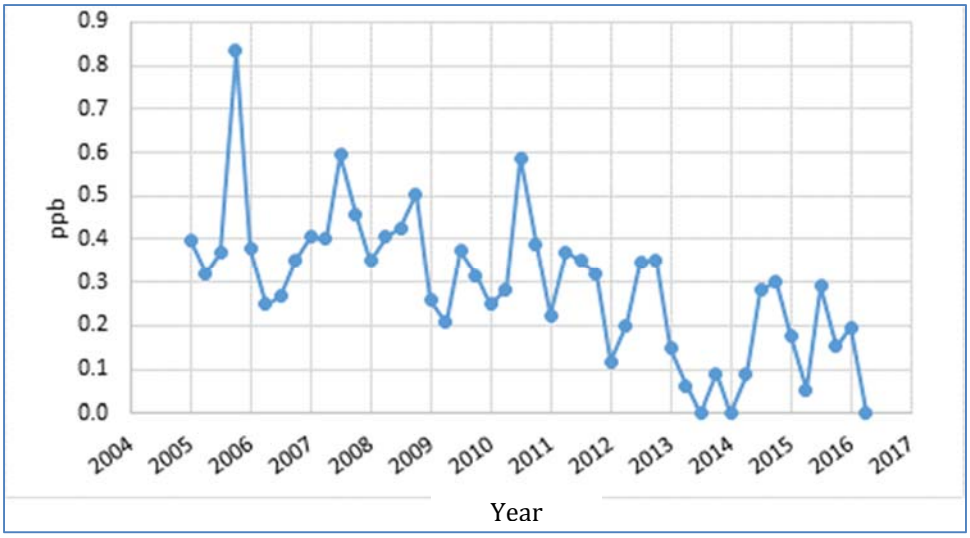
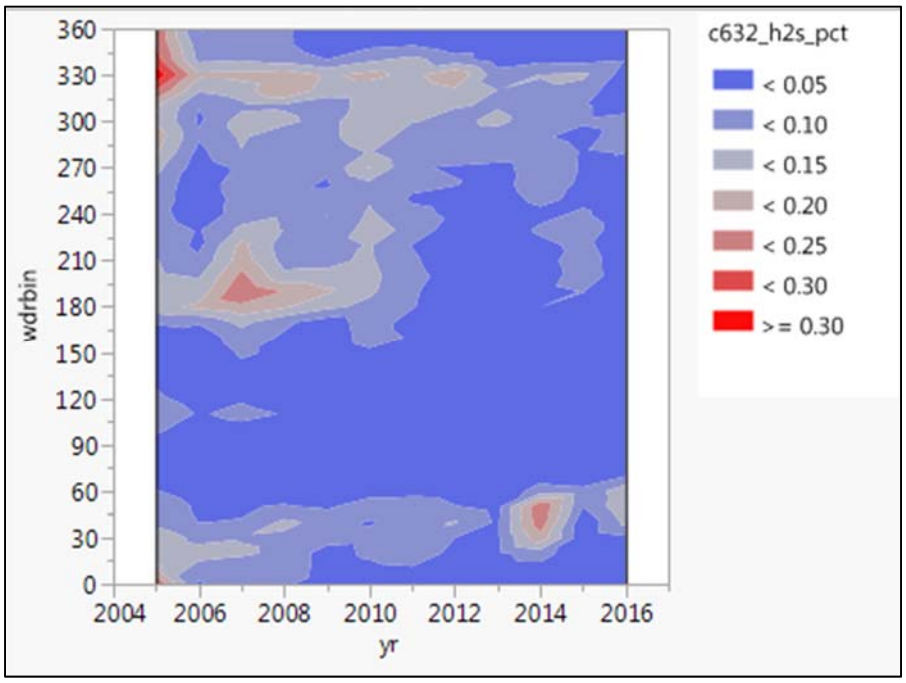


Figure 3-71. Contour plot of frequency that H_2S concentrations exceeded the 95th percentile 5-minute value for H_2S at FHR Easement CAMS 632



3.5.5 Solar Estates CAMS 633

Solar Estates CAMS 633 characteristics

The Solar Estates site was located at 9122 Leopard St, Corpus Christi, TX 78409, at latitude 27º 49' 45" North (27.8292º), longitude -97º 32' 37" West (-97.5436 º), and elevation 12.0 m. Although given a Leopard St address, the site was accessed at the end of Sunshine Ave. The site was recorded with the EPA site number 483550041, and TCEQ CAMS number 633. It was activated on December 1, 2004, and began producing data in mid-December. The site was only partially decommissioned on May 22, 2016, as the meteorological equipment and auto-GC continue to operate there under contract with the TCEQ as this report is being completed in 2017.

An aerial image of the site appears in Figure 3-72, below. The site is located with excellent exposure in an open farm field adjacent to a single-family neighborhood. Figure 3-73, page 3-58, shows a higher altitude aerial image with Solar Estates site along with formerly nearby sites FHR Easement CAMS 632 and West End Inner Harbor CAMS 631, and the currently operating TCEQ Tuloso CAMS 21 site.

Earlier in the report, Table 3-2, page 3-3, noted that Solar Estates, along with the J. I. Hailey CAMS 630 site, has the best exposure in terms of a lack of nearby obstructions to air flow. Figure 3-74, page 3-58, shows a histogram of the wind directions measured over 11.5 years at Solar Estates, and Figure 3-75, page 3-59, shows a histogram of the wind speeds.

Figure 3-72. Solar Estates 633 aerial view

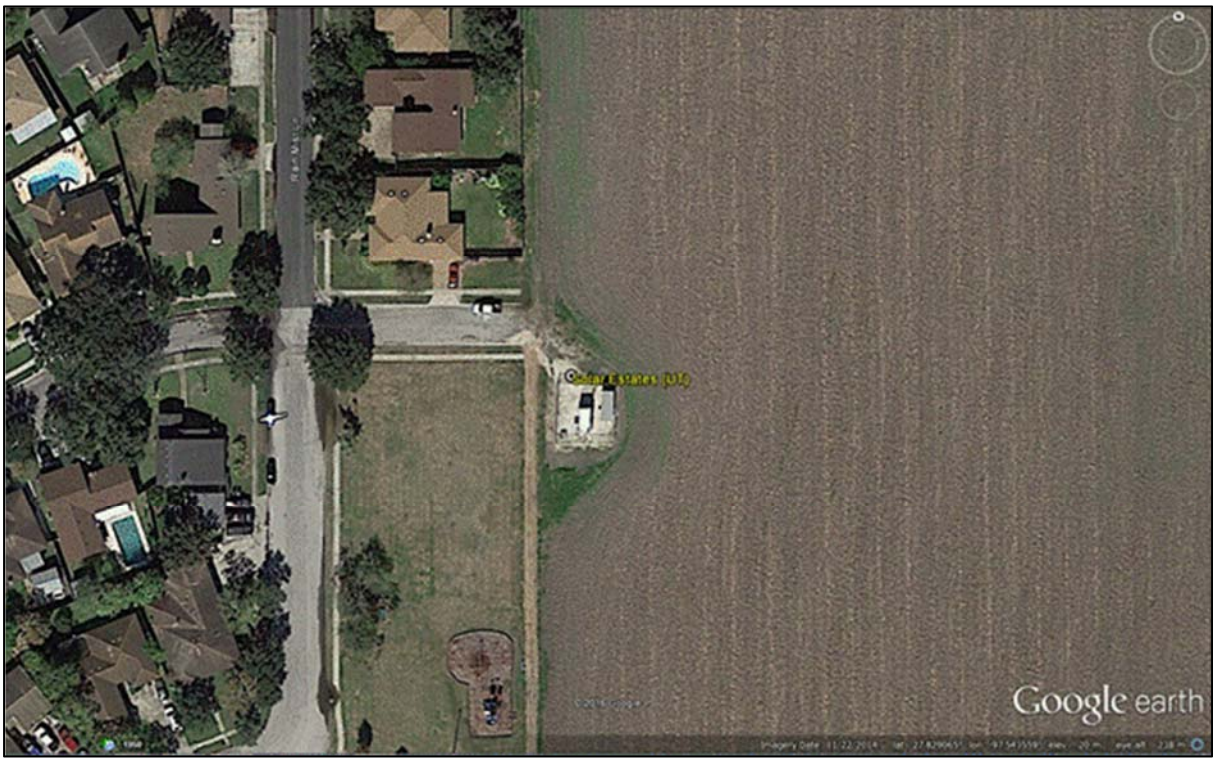


Figure 3-73. Solar Estates, FHR Ease., West End / Inner Harbor, TCEQ Tuloso aerial view from 4km

Figure 3-74. Solar Estates CAMS 633 wind direction distribution

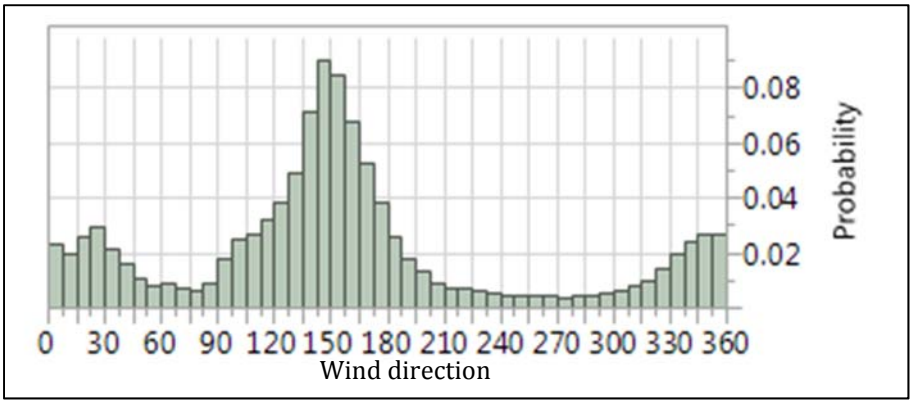
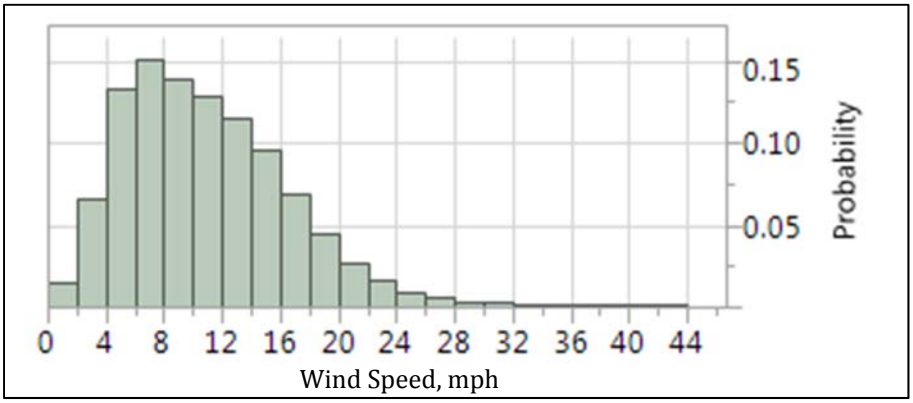


Figure 3-75. Solar Estates C633 wind speed distribution



Solar Estates CAMS 633 TNMHC

Figure 3-76, page 3-60, shows the time series for hourly TNMHC measurements from the Solar Estates site, which ended operating a TNMHC analyzer in 2012. Figure 3-77, page 3-60, shows the time series for the mean TNMHC concentration by quarter of the year. Concentrations declined after the first couple of years and then presented a relatively stable seasonal pattern until instrument decommissioning.

Figure 3-78, page 3-61, is a CPF contour plot of the frequency with which a TNMHC concentration exceeds the 95th percentile 5-minute value of 317 ppbC over the period of monitoring. The image is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows that the upper 5-percentile highest concentrations came from northeast, and the frequency declined but northeast was still the strongest direction of elevated concentrations up until the instrument decommissioning.

Figure 3-76. Time series for hourly TNMHC concentrations, ppbC units, Solar Estates CAMS 633 site

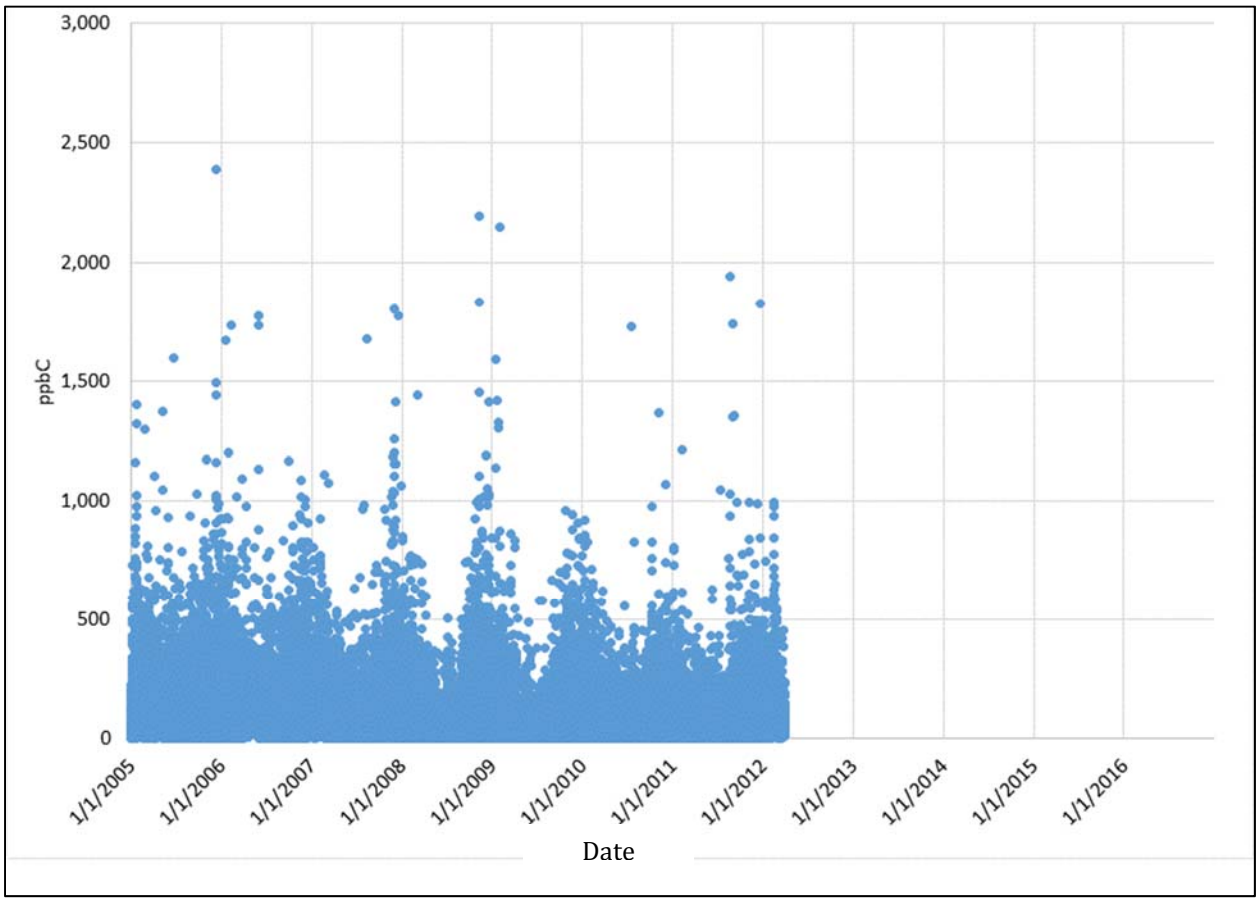


Figure 3-77. Solar Estates CAMS 633 TNMHC quarterly mean concentrations, Jan. 2005 – May 2012

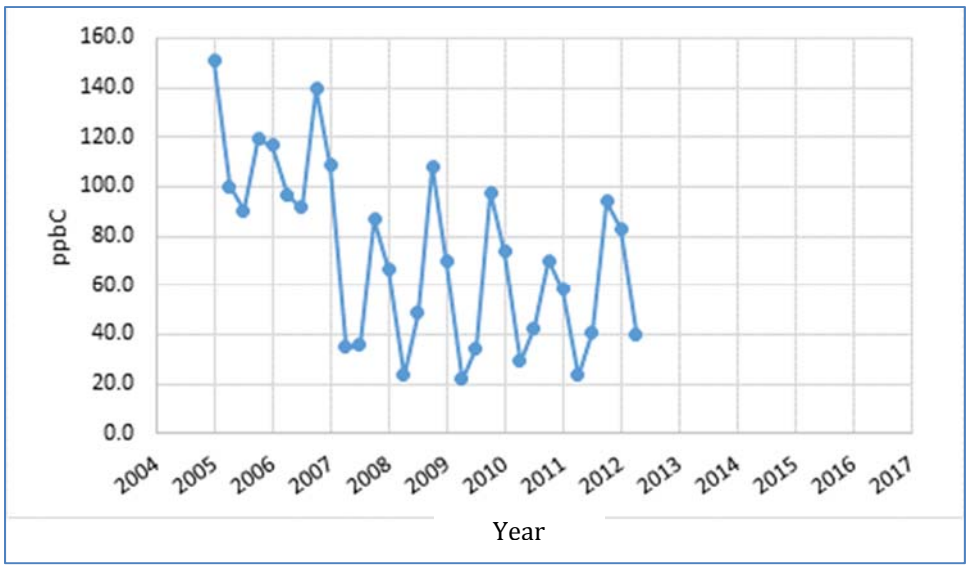
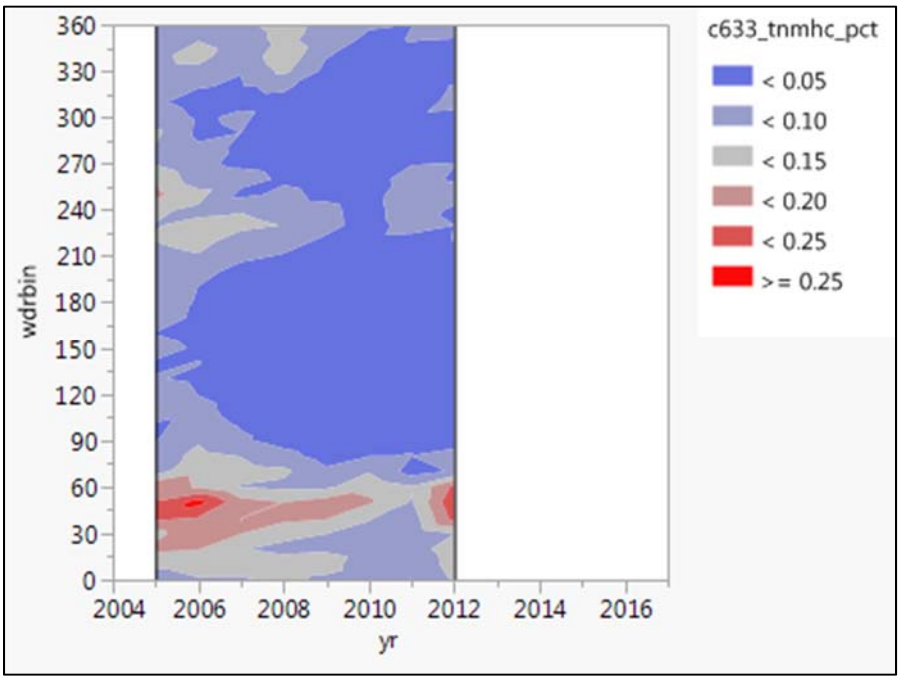


Figure 3-78. Contour plot of frequency that TNMHC concentrations exceeded the 95th percentile 5-minute value for TNMHC at Solar Estates CAMS 633



Solar Estates CAMS 633 SO_2

At Solar Estates, the SO_2 monitor was found to be affected by an apparent interferent. Figure 3-79, page 3-62, shows the time series for hourly SO_2 measurements. There appear to be three distinct periods of elevated concentrations that stand out. This issue is discussed in significant detail later in this chapter beginning on page 3-74. Figure 3-80, page 3-62, shows a graph of the mean SO_2 concentration by quarter of the year.

Figure 3-81, page 3-63, is a CPF contour plot of the frequency with which an SO_2 concentration exceeded the 95th percentile 5-minute value of 1.6 ppb over the period of monitoring. The image in Figure 3-81 is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows that the highest rate of occurrence of concentrations in the upper 5 percent came from the easterly direction, and that over the last few years the frequency of upper 5 percentile values significantly declined. What is surprising about Figure 3-81 is that the highest SO_2 concentrations at Solar Estates, say those greater than 20 ppb in Figure 3-76, were measured under south-southeast winds. Figure 3-82, page 3-63, recasts the CPF contour plot for the frequency with which an SO_2 concentration exceeded the 99th percentile 5-minute value of 8.7 ppb over the period of monitoring. In Figure 3-82, for periods in 2012 and 2013, when winds blew between 150 and 180 degrees, an upper 1 percent value was measured more than 12 percent of the time.

Figure 3-79. UT CAMS 633 Solar Estates SO_2 time series, Dec. 2004 – May 2016 – believed to have been affected by an interferent pollutant in early 2005, late 2007-early 2007, 2011 - 2013

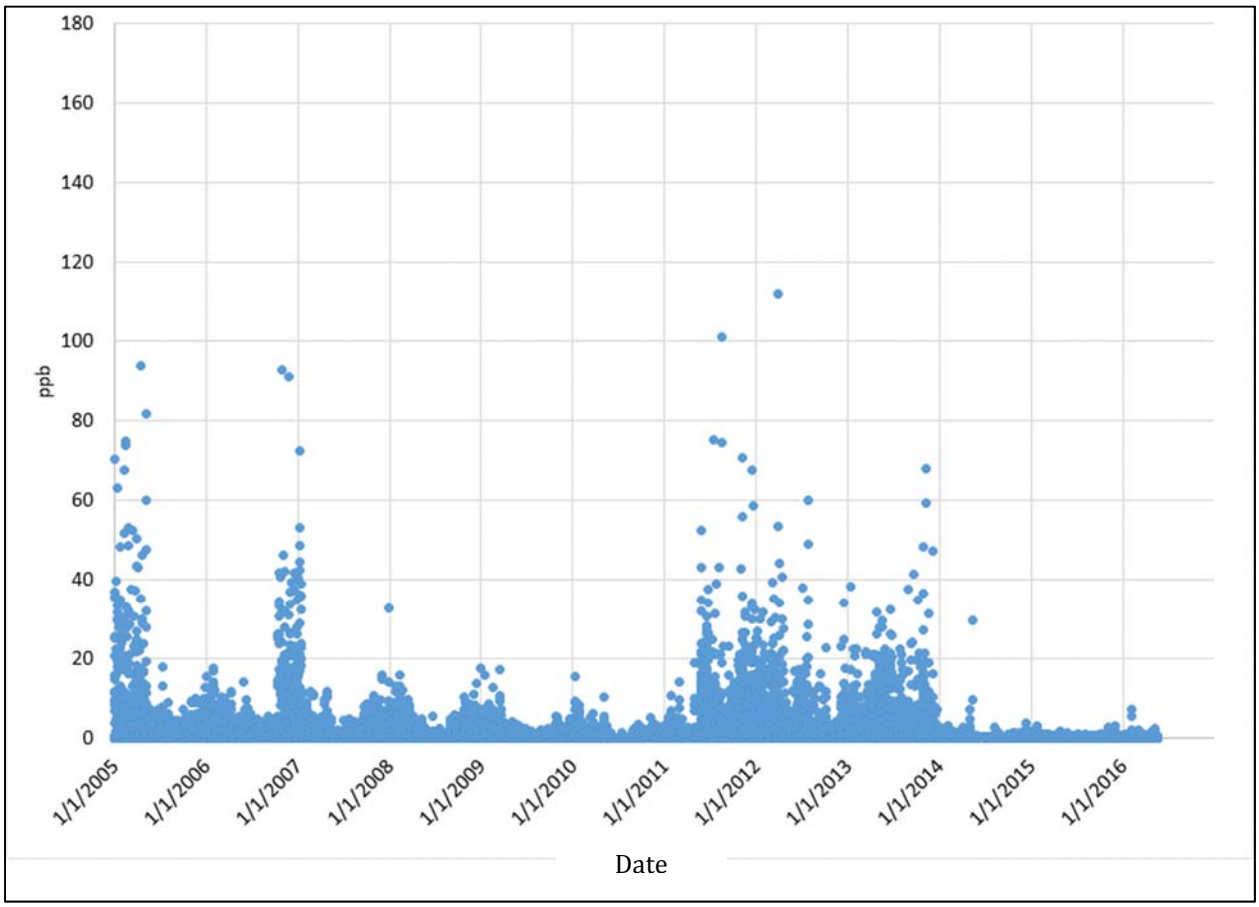


Figure 3-80. Solar Estates CAMS 633 SO_2 quarterly mean concentrations, Jan. 2005 – May 2016

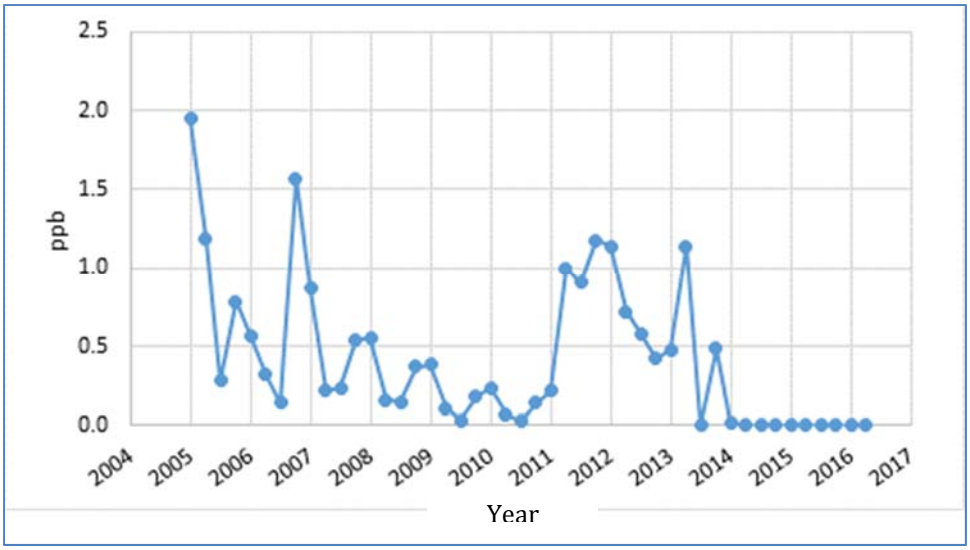


Figure 3-81. Contour plot of frequency that SO_2 concentrations exceeded the 95th percentile 5-minute value for SO_2 at Solar Estates CAMS 633

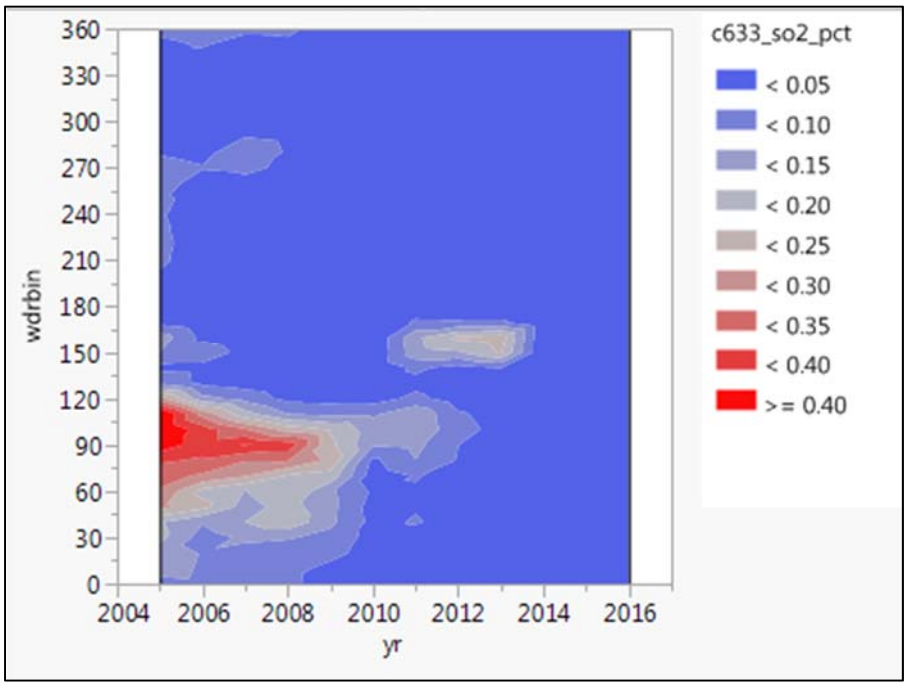
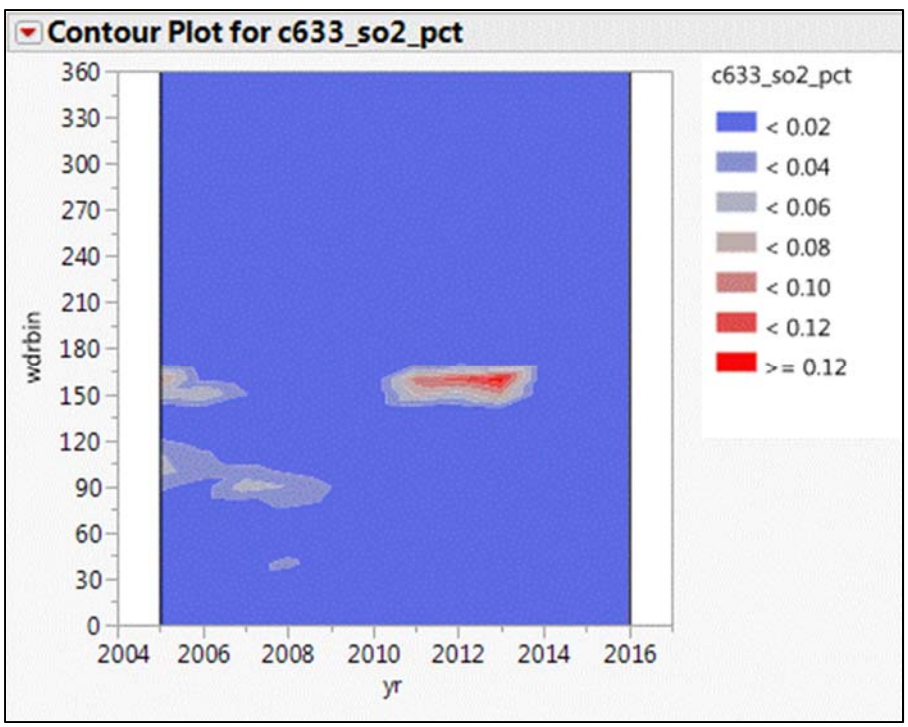


Figure 3-82. Contour plot of frequency that SO_2 concentrations exceeded the 99th percentile 5-minute value for SO_2 at Solar Estates CAMS 633



Solar Estates CAMS 633 H_2S

Figure 3-83, below, shows the time series for hourly H_2S measurements. Figure 3-84, page 3-65, shows a graph of the mean H_2S concentration by quarter of the year. Figure 3-84 suggests that not until 2016 were concentrations close to 0.0 ppb on average.

Figure 3-85, page 3-65, is a CPF contour plot of the frequency with which an H_2S concentration exceeded the 95th percentile 5-minute value of 1.1 ppb over the period of monitoring. The image in Figure 3-85 is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows that the highest rate of occurrence of concentrations in the upper 5 percent came from the north-northwest direction, and that recently the frequency of upper 5 percentile values declined.

Figure 3-83. Time series for hourly H_2S concentrations, ppb units, Solar Estates CAMS 633 site

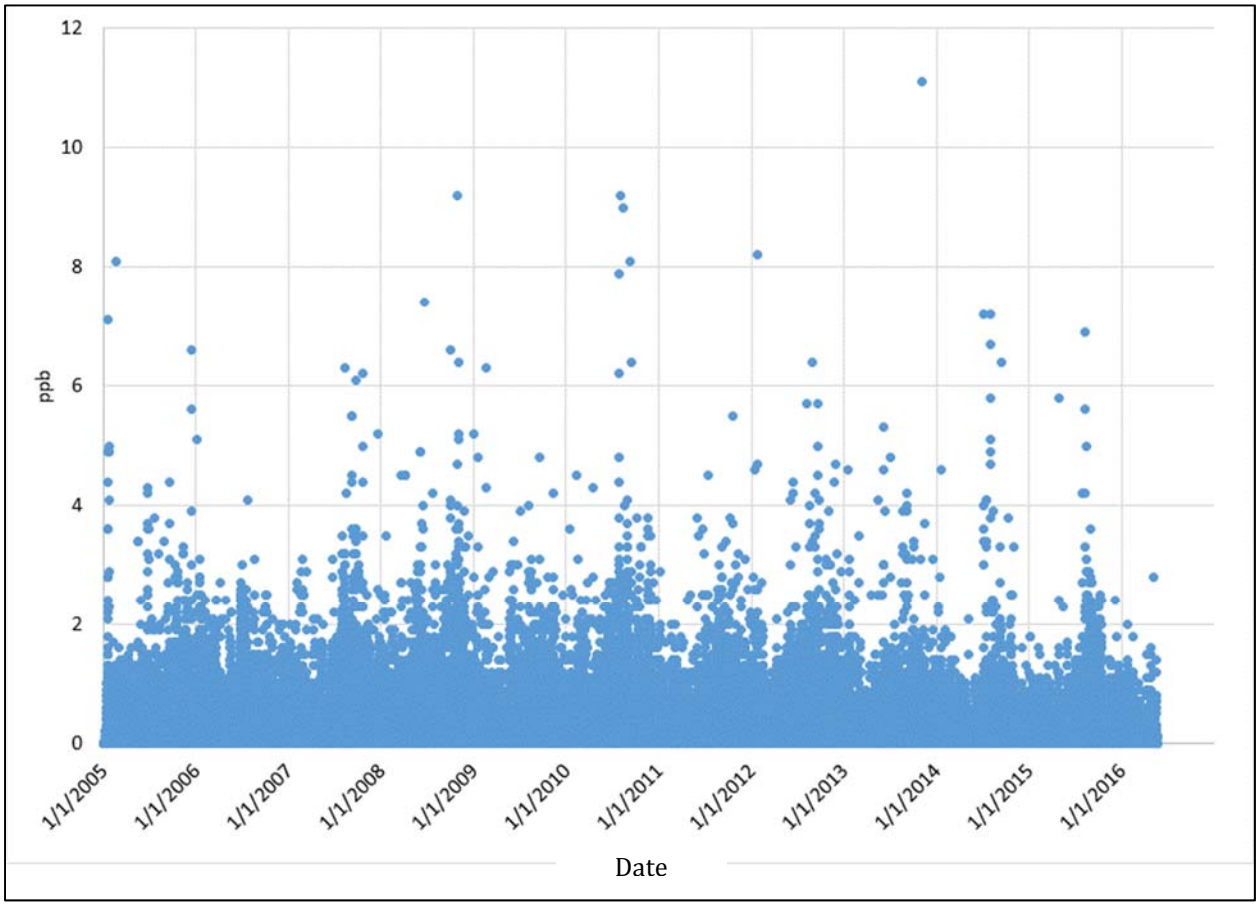


Figure 3-84. Solar Estates CAMS 633 H_2S quarterly mean concentrations, Jan. 2005 – May 2016

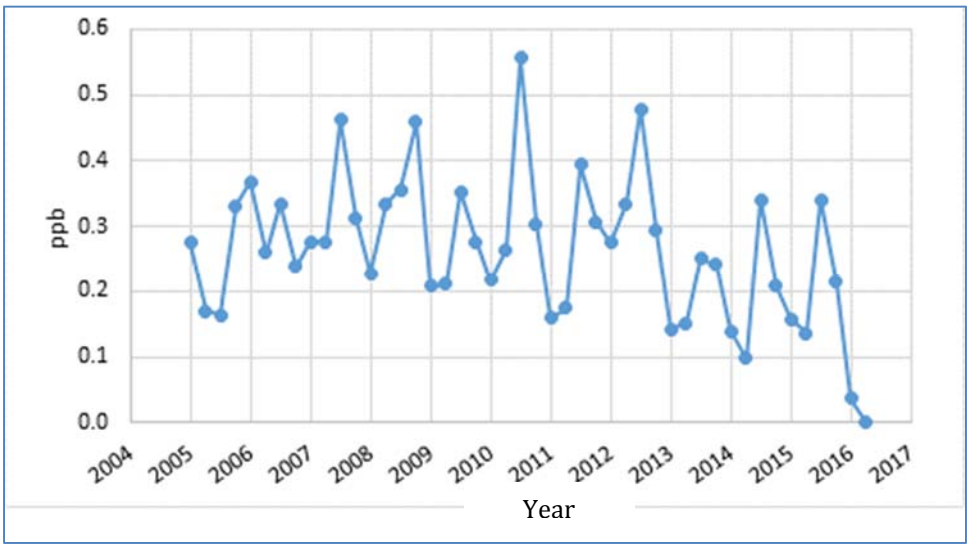
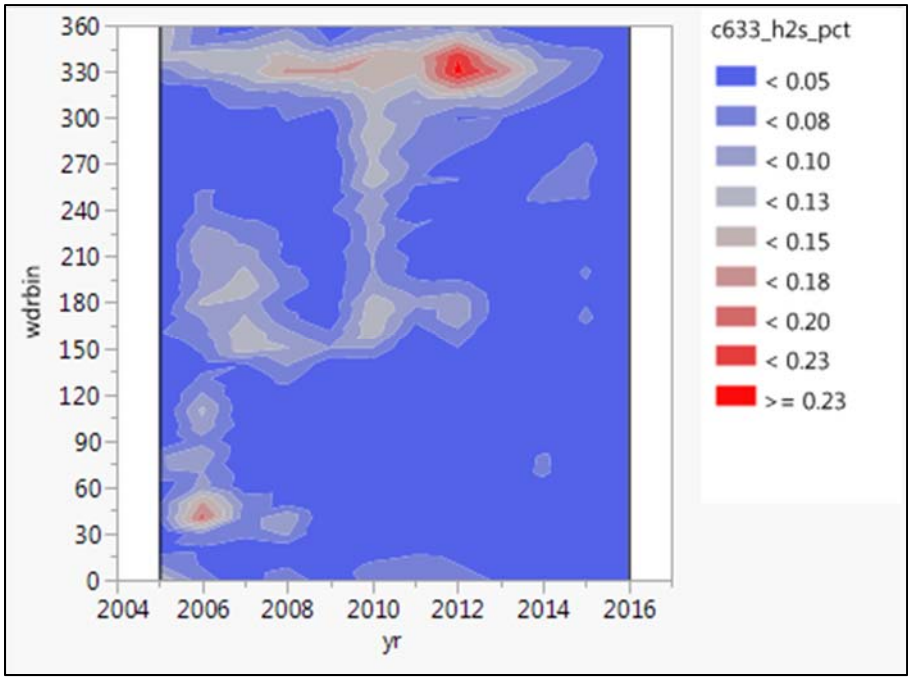


Figure 3-85. Contour plot of frequency that H_2S concentrations exceeded the 95th percentile 5-minute value for H_2S at Solar Estates CAMS 633



Solar Estates Auto-GC

The Solar Estates site housed an automated gas chromatograph (auto-GC) instrument, which continues operating at the site under contract with the TCEQ. The auto-GC measures 46 hydrocarbon species on an hourly basis, using two to three hours each day for blank and gas standard runs for quality assurance. Although the instrument measures 46 species, in this project only 27 are reported on. Figures 3-86 to 3-89, pages 3-68 to 3-71 show the quarterly averages for these species over the period of the project, with the species divided among classes of species. Concentrations in these figures are shown in ppbC units, which allows better resolution for the heavier compounds that appear in lower volumetric concentrations but have more mass per mole. Hydrocarbons measured in ppbC can also be combined to compare with measurements from the TNMHC instrument.

Alkanes, which are stable, less reactive species that tend to comprise the largest faction of mass among the nonmethane hydrocarbons, are shown in Figure 3-86, page 3-68. From 2005 to 2011, mean concentrations for all alkanes had a downward trend. However, from 2011 to 2015 the alkane mean concentrations for ethane, propane, and several other species increased during the first and fourth quarters, with a decrease in the fourth quarter of 2015 and first quarter of 2016.

Benzene, ethylbenzene, toluene, and xylene-isomers are grouped as BTEX compounds and shown in Figure 3-87, page 3-69. These species, for which there are toxicological concerns, have had a downward trend, flattening out in recent years.

Figure 3-88, page 3-70, shows the quarterly means for alkene species, which are more chemically reactive in the air and of concern with regard to ozone formation. These species generally show no significant trend, but are measured at very low concentrations. One species, 1,3-butadiene, is an air toxic compound and has significantly declined after one industrial source thought to be the primary emitter for the species changed operations and no longer emitted measurable 1,3-butadiene.

The heaviest species measured are in the nine to ten carbon range and are generally associated with heavy-duty truck emissions. Despite their heavier mass, they are measured in the lowest concentrations, as shown in Figure 3-89, page 3-71. These species have shown a downward trend over time.

Figures 3-86 through 3-89 were plotted with a y-axis scale to match the y-axis scale used later in this chapter in graphs of the Oak Park CAMS 634 auto-GC data.

Figure 3-90, page 3-72, shows the time series for hourly benzene concentrations in ppbV units that are comparable to TCEQ's AMCVs. Concentrations overall have declined, as was shown in Figure 3-87, although the highest one hour value measured to date at 13.8 ppbV was on October 3, 2014, at 18 CST.

Figure 3-91, page 3-73, shows the time series for hourly 1,3-butadiene concentrations in ppbV units that are comparable to TCEQ's AMCVs. The data have been filtered to only use measurements under coincident winds from the south through west-northwest. Concentrations declined relatively suddenly in late 2009 when the upwind industrial facility thought to be the

emission source changed ownership. Despite the elevated concentrations, the peak concentration was 35.5 ppbV, well below the TCEQ AMCV of 230 ppbV for odor or 1,700 ppbV for health.

Figure 3-86. Solar Estates CAMS 633 auto-GC alkane species quarterly means March 2005 – May 2016

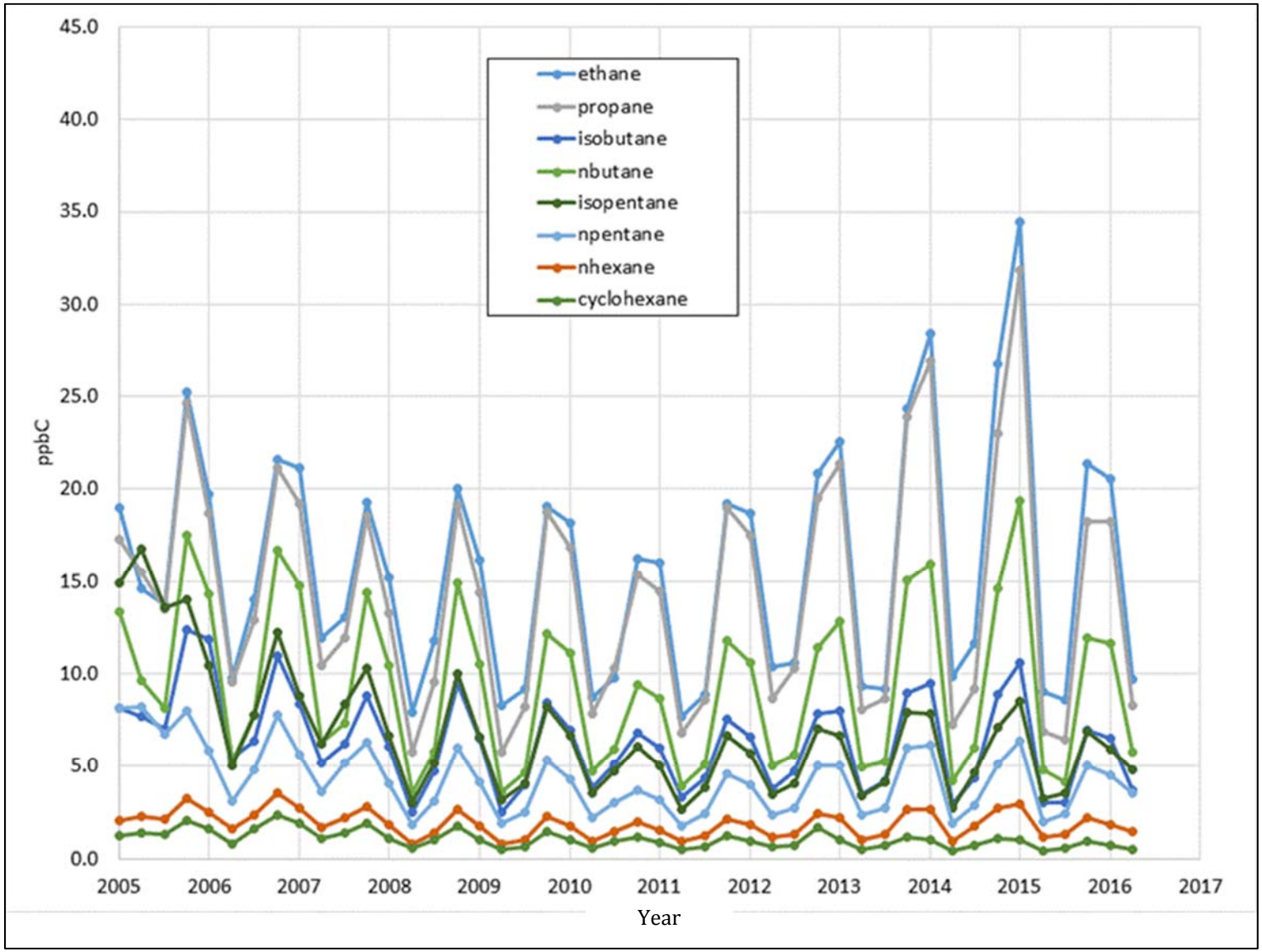


Figure 3-87. Solar Estates CAMS 633 auto-GC BTEX species quarterly means March 2005 – May 2016

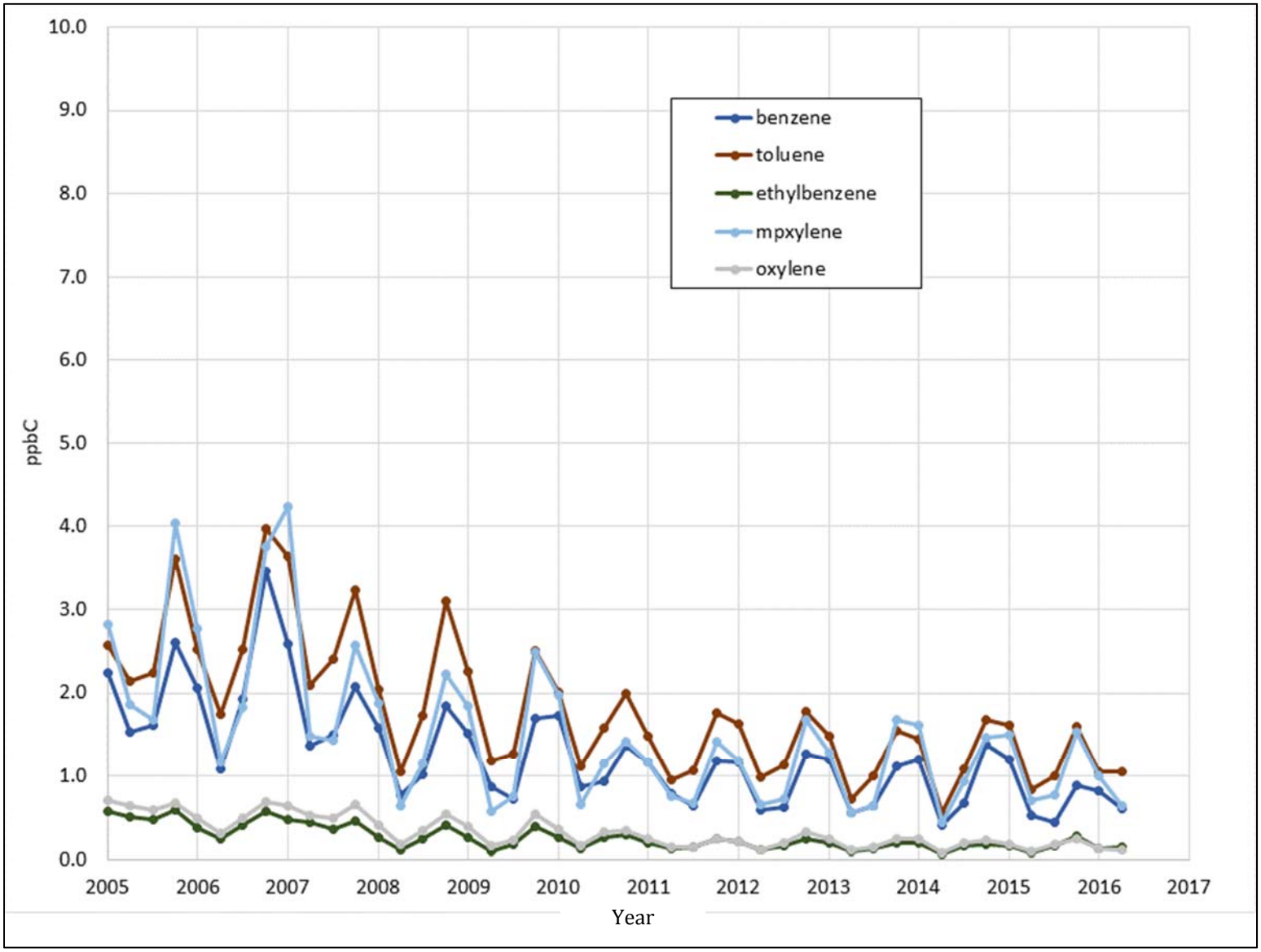


Figure 3-88. Solar Estates CAMS 633 auto-GC alkene species quarterly means March 2005 – May 2016

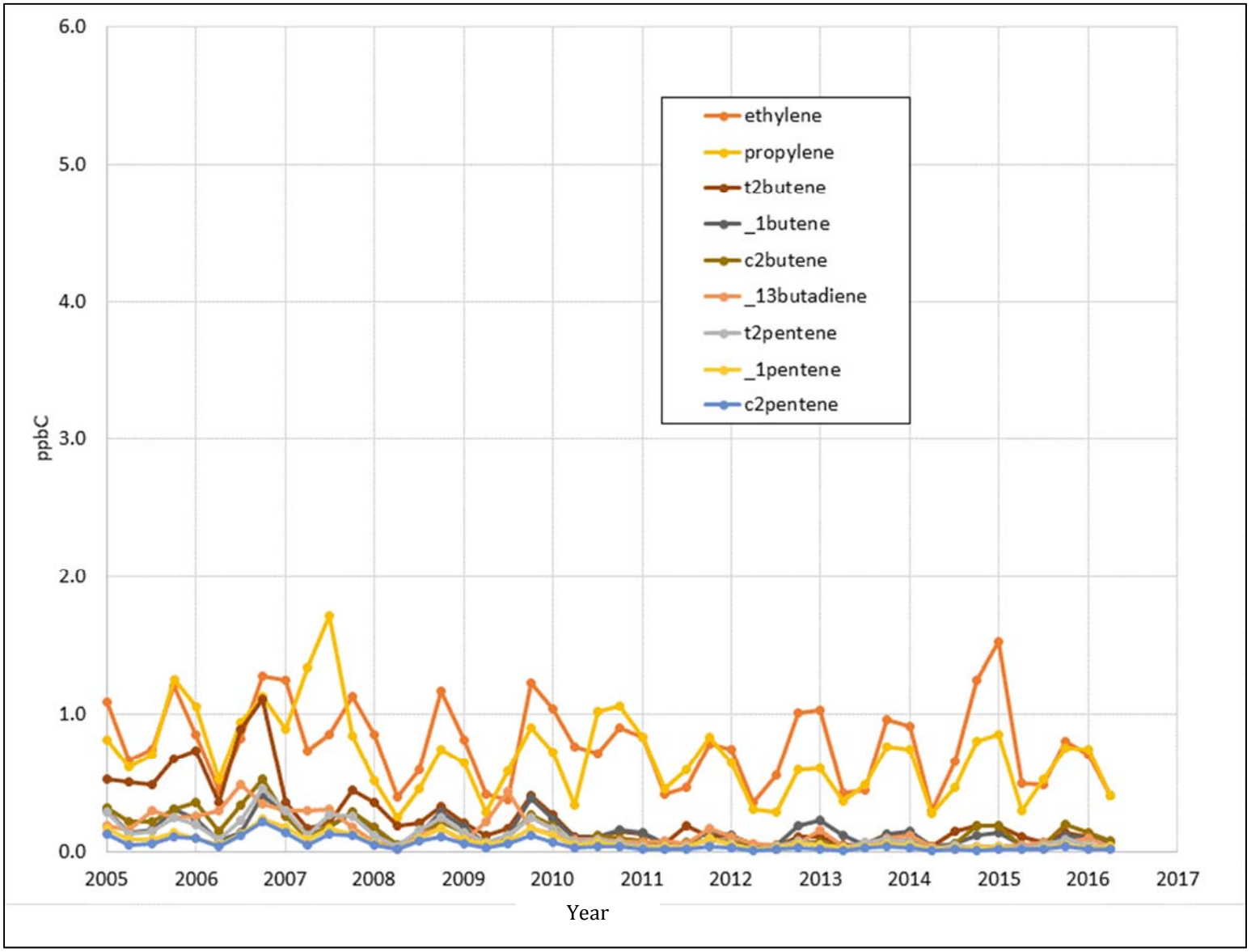


Figure 3-89. Solar Estates CAMS 633 auto-GC C9 – C10 species quarterly means March 2005 – May 2016

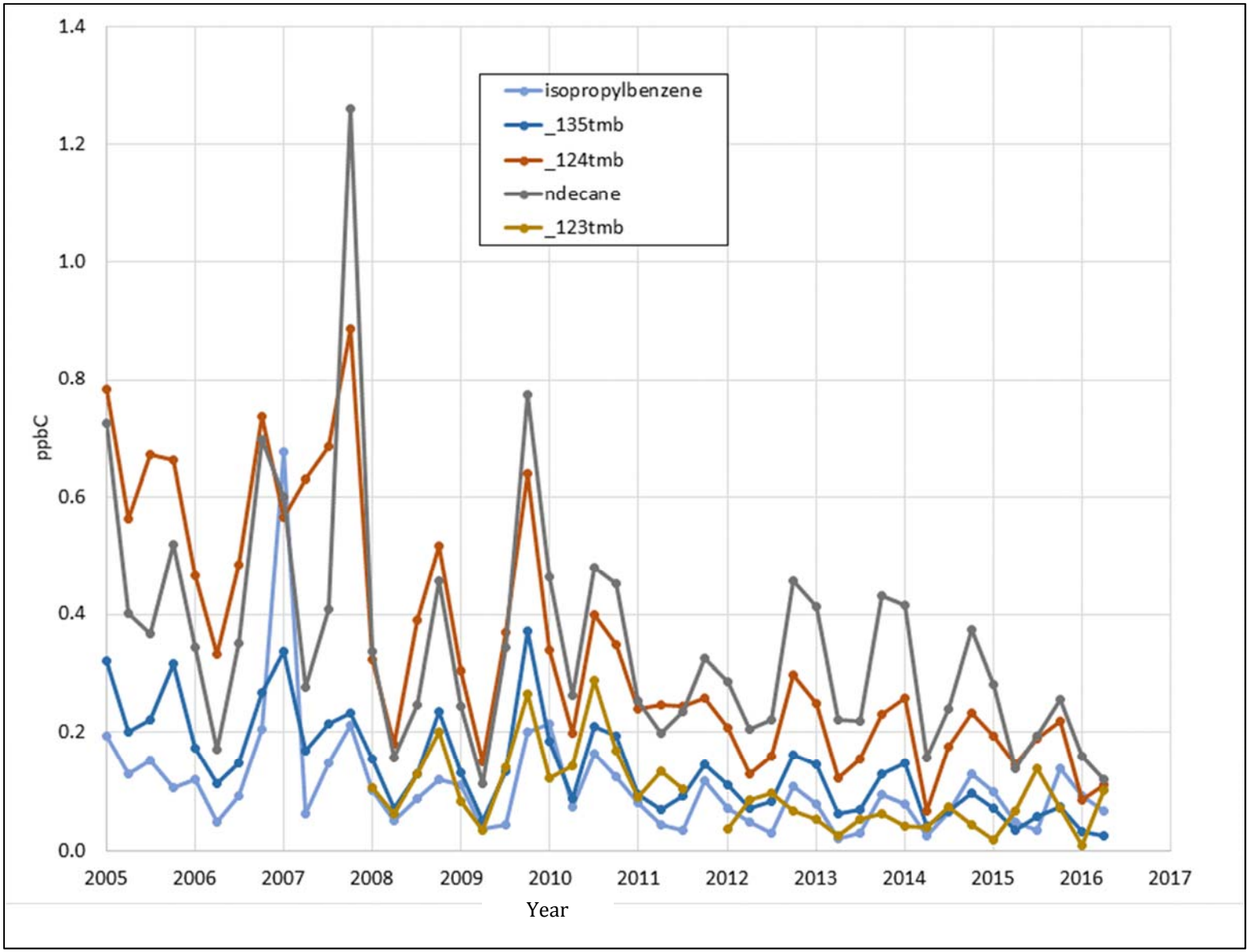


Figure 3-90. Solar Estates CAMS 633 benzene ppbV units, 3/1/2005 – 5/21/2016

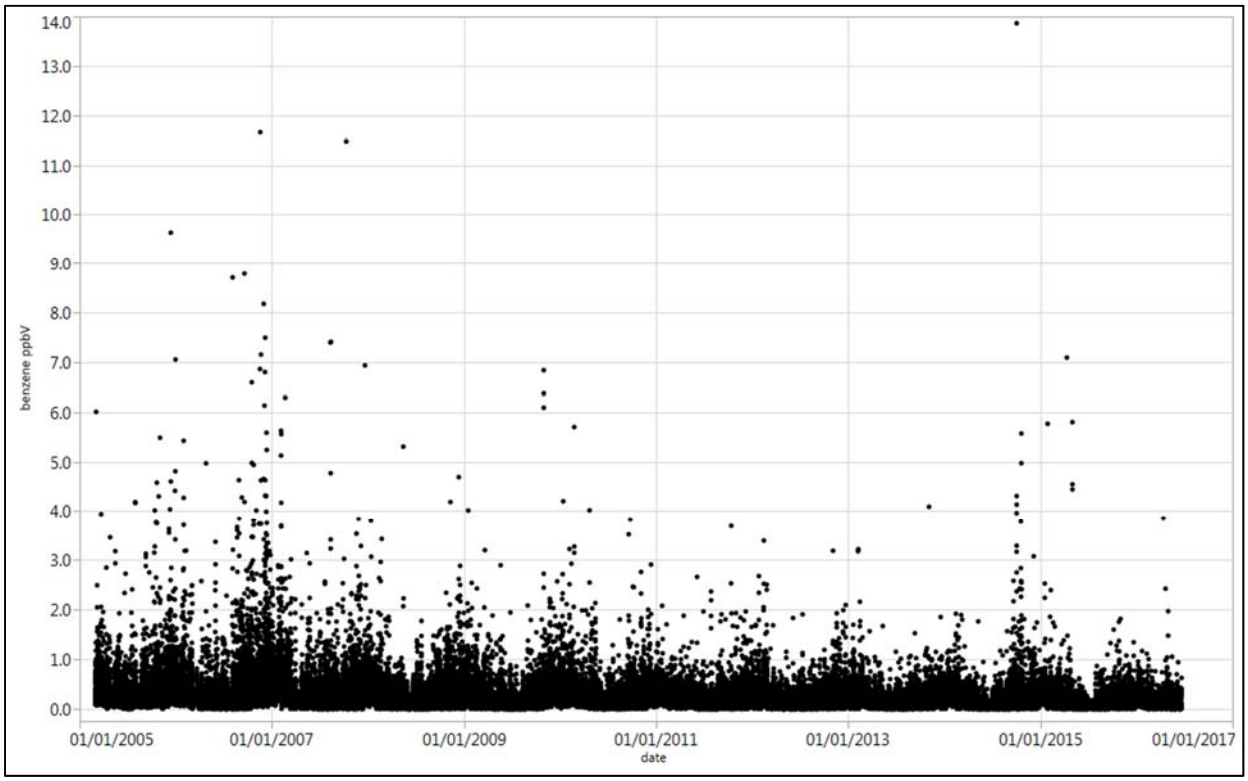
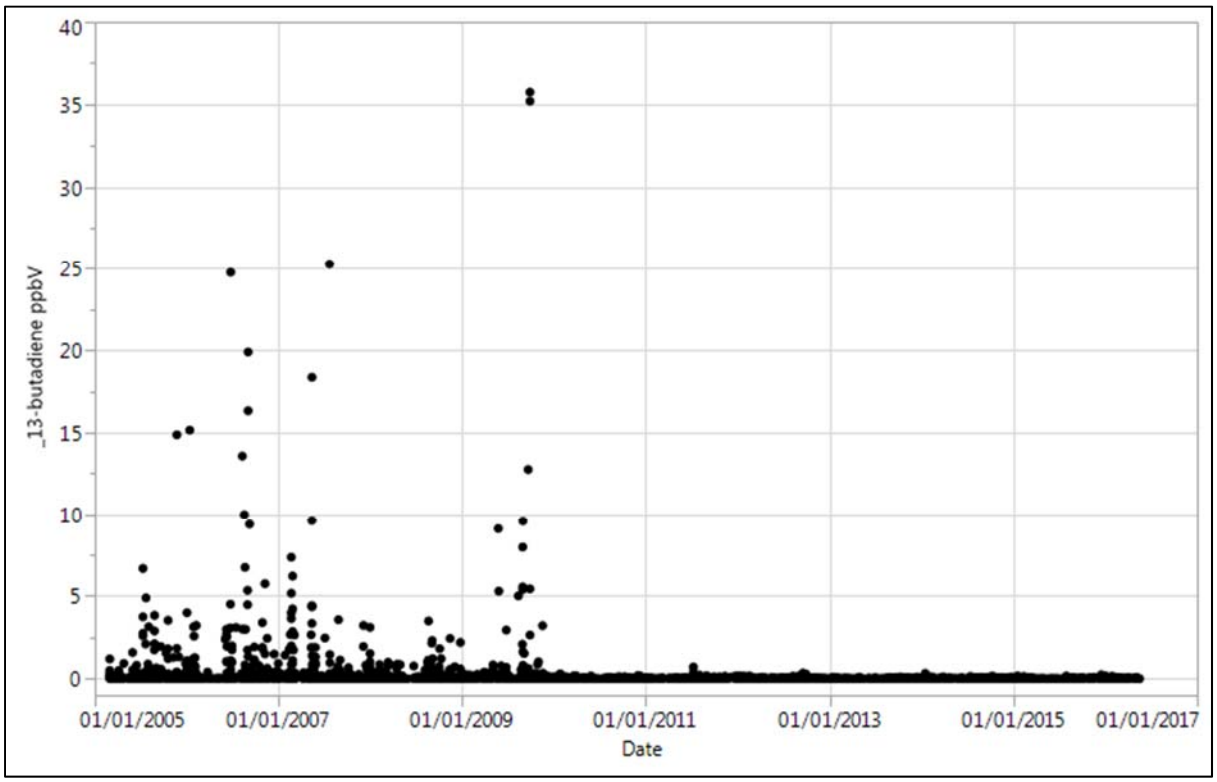


Figure 3-91. Solar Estates CAMS 633 1,3-butadiene ppbV, winds south to west-northwest 3/1/2005 – 5/21/2016



Sulfur dioxide interferent at Solar Estates and Flint Hills Resources Easement
<u>Ambient data</u>

Concentrations of SO_2 intermittently had been measured that exceed the one-hour 75 ppb level of the 2010 National Ambient Air Quality Standards (NAAQS) for SO_2 at Solar Estates CAMS 633 since the project began. Elevated SO_2 at Solar Estates had primarily been associated with the following conditions:

- A narrow range of wind directions, from the southeast between 135 and 180 degrees, with the highest average concentration at 156 degrees;
- Mondays through Fridays, and an occasional Saturday, particularly on weekends near major holidays;
- After 5 a.m. local time to around 6 p.m. local time (with adjustment made at changes between daylight savings and standard time);
- Occurring within three distinct periods since monitoring began: pre-2005 to May 11, 2005, October 5, 2006, to January 12, 2007, and May 25, 2011, to late December 2013.

Figure 3-92, page 3-75, shows the time series for 5-minute time scale SO_2 at Solar Estates from January 2005 to May 2016. Figures 3-93 to 3-104, pages 3-76 to 3-77, are arranged in a table to show the 5-minute Solar Estates SO_2 values by wind direction by year. Note that the y-axis scales are different in Figures 3-93 to 3-104. As the graphs show, the highest concentrations at Solar Estates for SO_2 were observed under a southeast wind, although another source appears to be at about 30 degrees and one at 90-105 degrees. The peak direction for elevated SO_2 was close to 156 degrees, and elevated values from this direction appeared in 2004, 2005, 2006, 2007, 2011, 2012, and 2013, but not in other years.

Corroborating concentrations from the southwest direction conforming to the temporal conditions listed above were measured at the Flint Hills Resources Easement site. Southwest winds in Corpus Christi tend to be light and variable and this is the least frequent wind direction in the area. Nevertheless, joint directionality analysis with Solar Estates and FHR data suggested the same emission source affected both sites, and said source was most likely located near Leopard St. Figure 3-105, page 3-78, shows SO_2 data from the FHR site over the April 18 – June 29, 2012, period graphed as a time series and as a function of wind direction. The graph on the right shows that the highest values arrived under southwesterly winds (indicated in the rectangle in the graph), and the graph on the left shows that these elevated concentrations were measured on three days. The highlighted time periods are: Friday April 20, 2012, 7:00 – 7:20 CST, Friday May 18, 2012, 6:05 – 8:00 CST, and Tuesday May 22, 2012, 6:55 – 7:00 CST. SO_2 values greater than 10 ppb are highlighted in Figure 3-105, page 3-78.

All the FHR SO_2 April 18 – June 29, 2012, five-minute data have been pooled into the average SO_2 concentration by wind direction (30-degree bins) and the percentage of SO_2 values in the upper 5 percentile (CPF > 95th percentile) by wind direction in Figure 3-106. Figure 3-106 shows that about 30 percent of SO_2 observations associated with winds between 225 and 255 degrees (centered on 240 degrees) were in the upper 5 percentile of all observations, and this wind bin had the highest mean concentration. This analysis shows that another Thermo-43C monitor at a different site configured and operated like Solar Estates also measured SO_2 from what is likely the same emissions source as the one affecting Solar Estates. Figure 3-107, page 3-79, shows an aerial map of the two sites with the hypothesized emission source location.

Figure 3-92. Elevated SO_2 at Solar Estates (and to lesser extent at FHR) occurred in three distinct periods: pre-2005 to May 11, 2005, October 5, 2006, to January 12, 2007, and May 25, 2011, to late December 2013

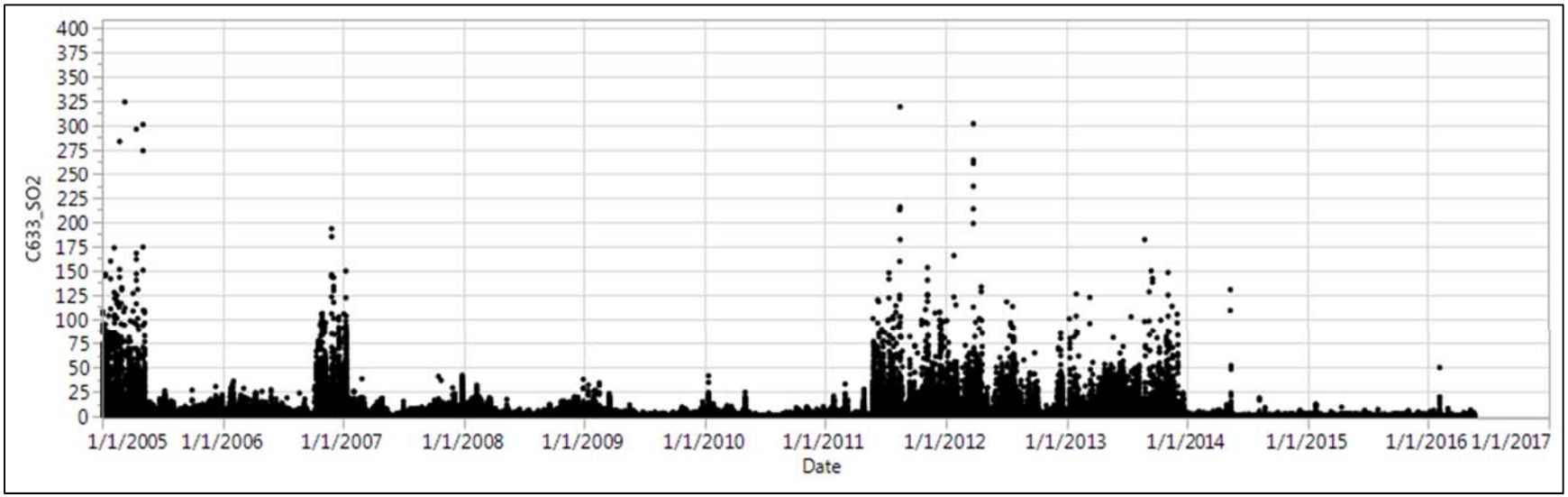


Figure 3-93. Solar 2015 SO_2 ppb by wind dir

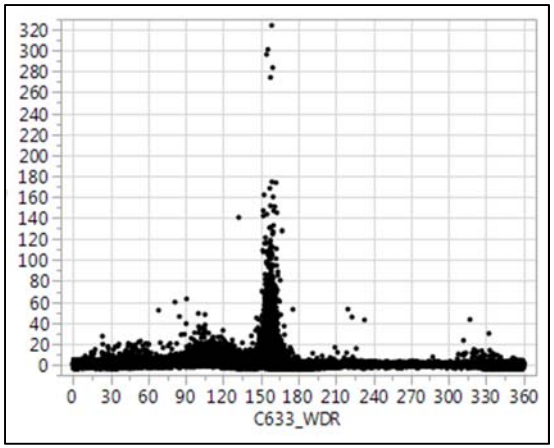


Figure 3-94. Solar 2006 SO_2 ppb by wind dir

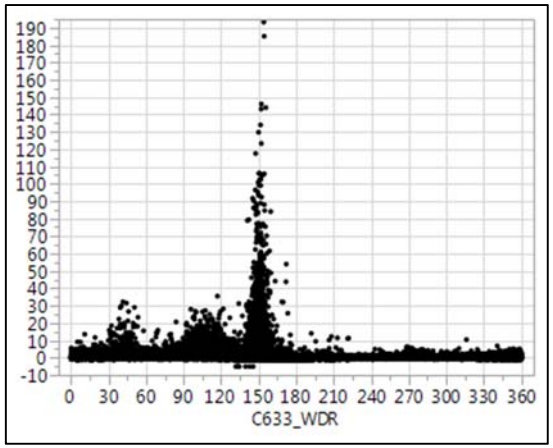


Figure 3-95. Solar 2007 SO_2 ppb by wind dir

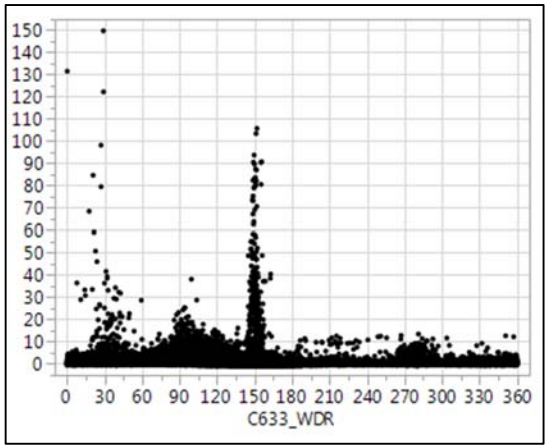


Figure 3-96. Solar 2008 SO_2 ppb by wind dir

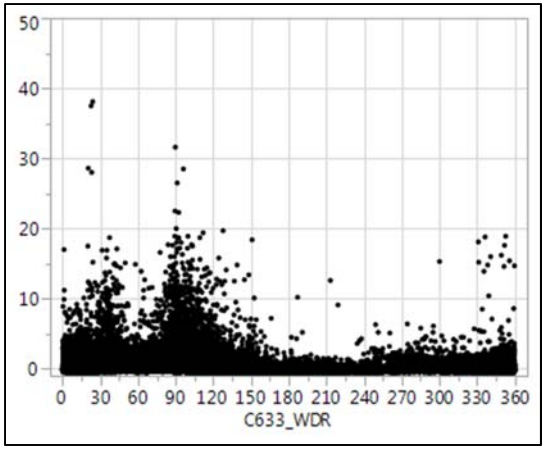


Figure 3-97. Solar 2009 SO_2 ppb by wind dir

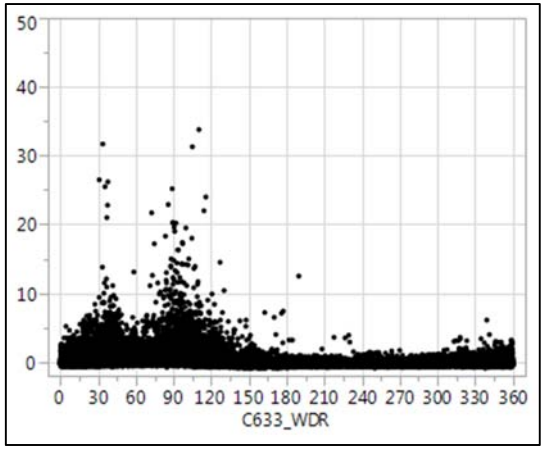


Figure 3-98. Solar 2010 SO_2 ppb by wind dir

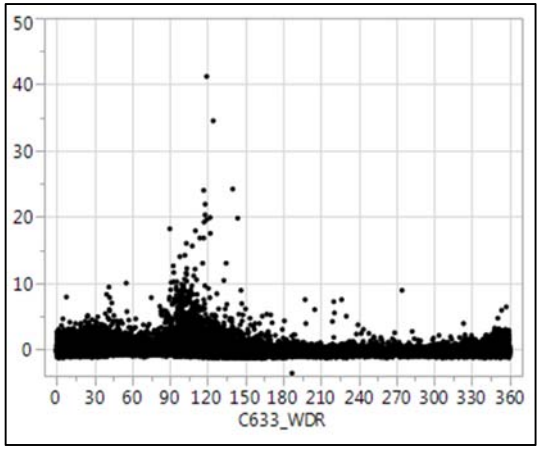


Figure 3-99. Solar 2011 SO_2 ppb by wind dir

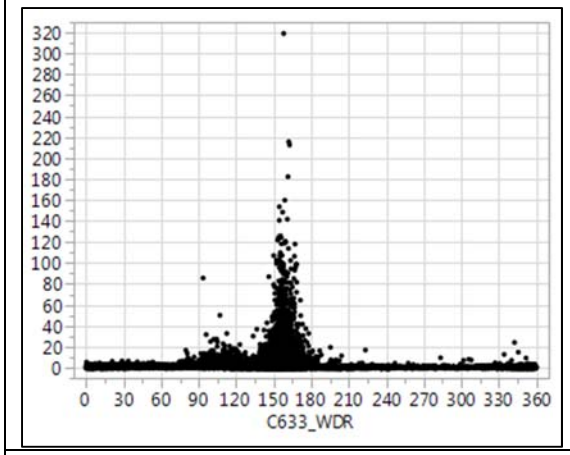


Figure 3-100. Solar 2012 SO_2 ppb by wind dir

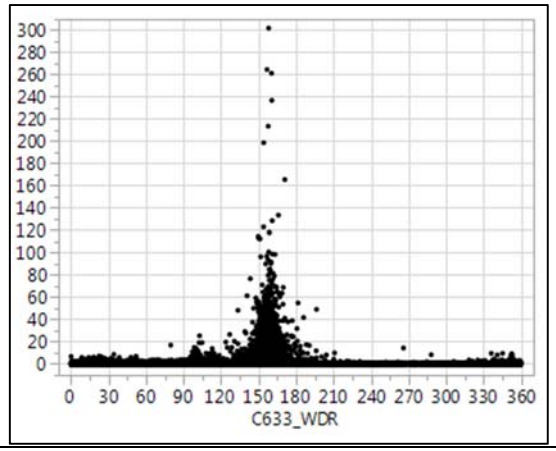


Figure 3-101. Solar 2013 SO_2 ppb by wind dir

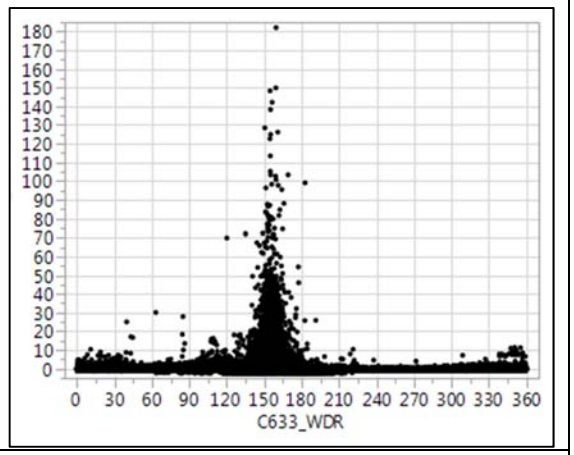


Figure 3-102. Solar 2014 SO_2 ppb by wind dir

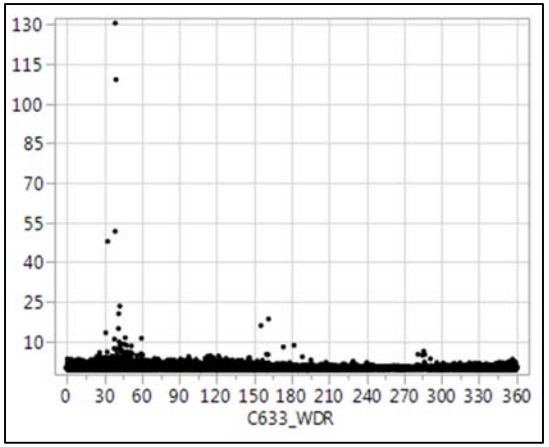


Figure 3-103. Solar 2015 SO_2 ppb by wind dir

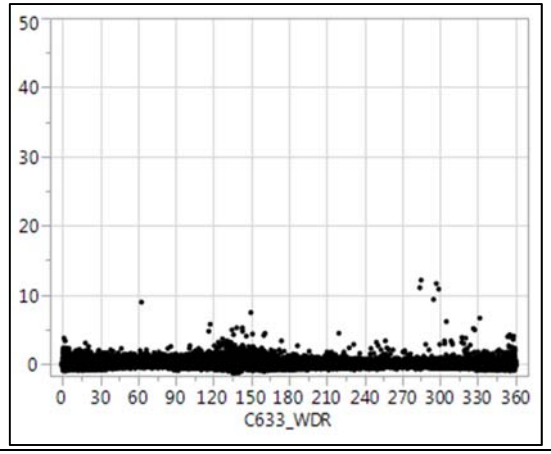


Figure 3-104. Solar 2016 SO_2 ppb by wind dir

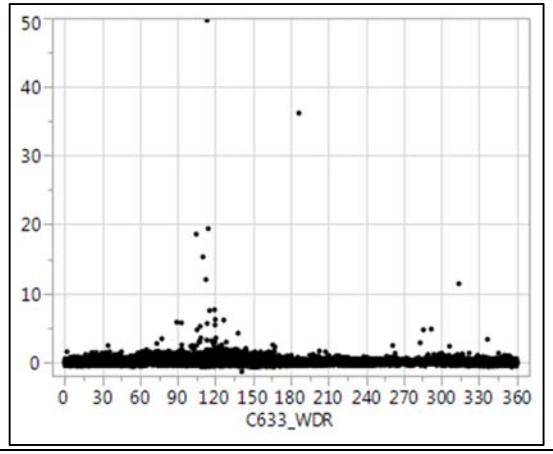


Figure 3-105. FHR CAMS 632 time series for SO_2 graphed on left, and graphed vs. wind direction on right. SO_2 values greater than 10 ppb are highlighted.

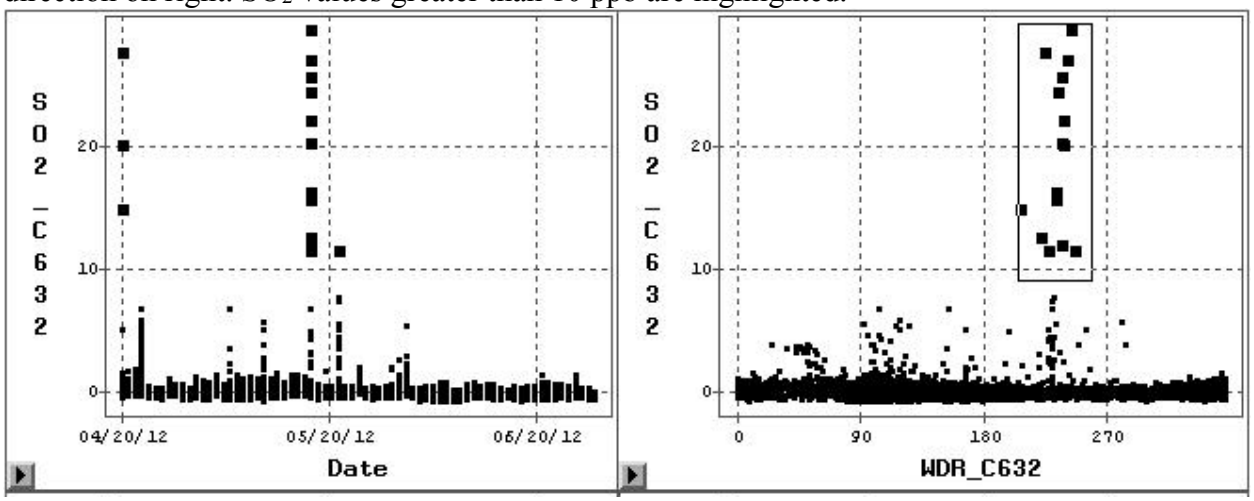


Figure 3-106. FHR CAMS 632 April 18 – June 29, 2012, mean SO_2 and conditional probability for exceeding 95th percentile by 30-degree wind direction bin

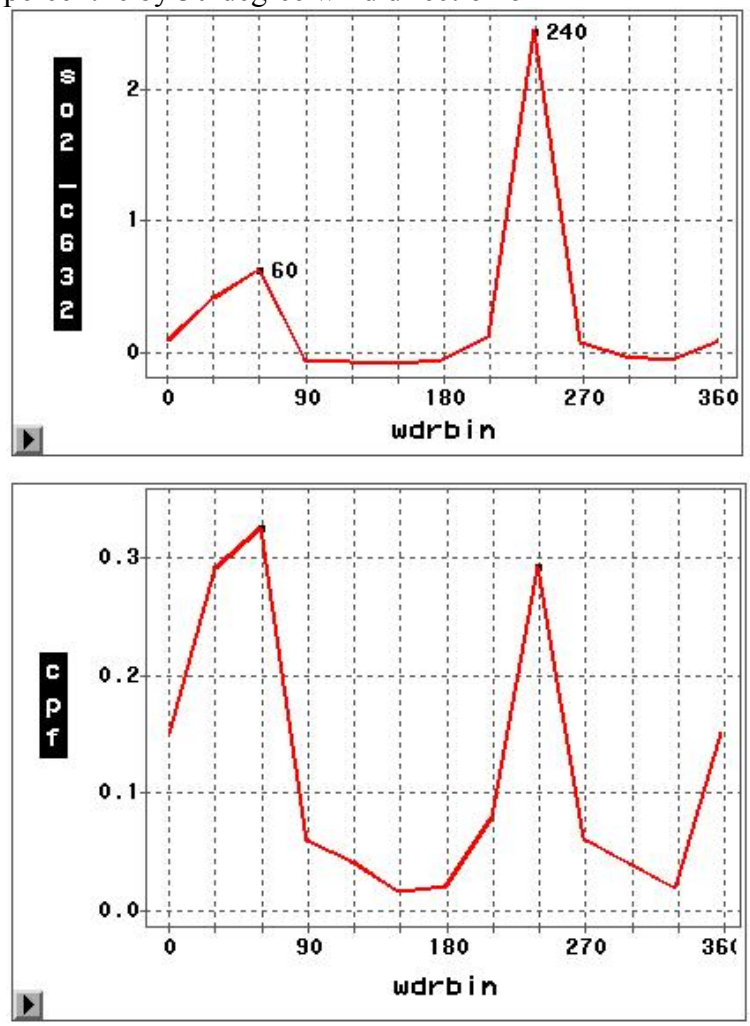


Figure 3-107. Aerial map of three CAMS sites and SO_2 point sources in the 2008 TCEQ emissions inventory and the suspected emissions source

TCEQ agreed that they did not expect an SO_2 source to be found upwind to the southeast of the Solar Estates site. TCEQ staff and UT Austin staff met with personnel from the possible source industry on April 27, 2012, and the industry personnel provided details to TCEQ about their operations. No conclusions could be reached. Some SO_2 might have been produced by diesel engines in heavy-duty trucks, but this was not believed to be enough to detect at Solar Estates.

The facts that

1. the nearby TCEQ Tuloso CAMS 21 SO_2 monitor did not detect SO_2 from a direction in accordance with the Solar Estates measurements, and the Solar Estates instrument type was different from the CAMS 21 instrument model, and
2. the SO_2 monitor at the Project's Flint Hills Resources Easement CAMS 632 site did detect SO_2 from a direction consistent with the Solar Estates directions using the same model of instrument as that used at Solar Estates,

led to a question as to whether the instrument model was a factor. TCEQ agreed to participate in monitor colocation experiment to see if different models of instruments would agree in terms of SO_2 quantification in ambient air.

As was mentioned above, the nearby FHR Easement CAMS 632 site also observed elevated SO_2 concentrations (but no NAAQS exceedances) but under southwesterly winds.

Colocation experiment

Examination of the ambient data up to April 2012 led to a series of experiments performed at the Solar Estates CAMS 633 and TCEQ Tuloso CAMS 21 to attempt to determine assignable causes for the elevated SO_2 at Solar Estates. Additional SO_2 instruments were borrowed and deployed to the Solar Estates site and to the nearby Tuloso CAMS 21 site. The instrument arrangements used are shown in Table 3-4, below. TCEQ set up fictitious CAMS site 210 to record the collocated data.

Table 3-4. Monitoring configurations at CAMS 633 and 21, April 18 – June 29, 2012

Configuration nickname	Site	Normal station monitor	TCEQ CAMS 210 (POC 1)	UT CAMS 210 (POC 2)	Start	End
C633 ml9850	Solar 633	Thermo-43C	ML-9850	ML-9850	4/18/12	5/8/12
C633 teco43	Solar 633	Thermo-43C	ML-9850	Thermo-43C	5/9/12	6/13/12
C21 collocate	Tuloso 21	API-100A	ML-9850	Thermo-43C	6/13/12	6/29/12

The results were as follows:

- In the instrument collocation experiment at Solar Estates CAMS 633, all combinations of instrument models (two Thermo 43Cs and one ML9850; one Thermo 43C and two ML9850s) measured similar elevated SO_2 concentrations when the wind blew from the refinery areas, <u>but different instrument models measured different concentrations above background levels when winds blew from the direction of the suspect source during plant operating hours</u>.

- When the wind blew from the refinery areas, the nearby Texas Commission on Environmental Quality (TCEQ) Tuloso CAMS 21 site measured elevated SO_2, but when winds blew from the direction of the suspect source plant, the CAMS 21 site <u>did not measure</u> elevated SO_2. CAMS 21 housed an API-100A SO_2 monitor. During the collocation experiment at CAMS 21 the two additional monitors of different model types (one Thermo 43C and one ML9850) exhibited identical behavior to the CAMS 21 instrument.

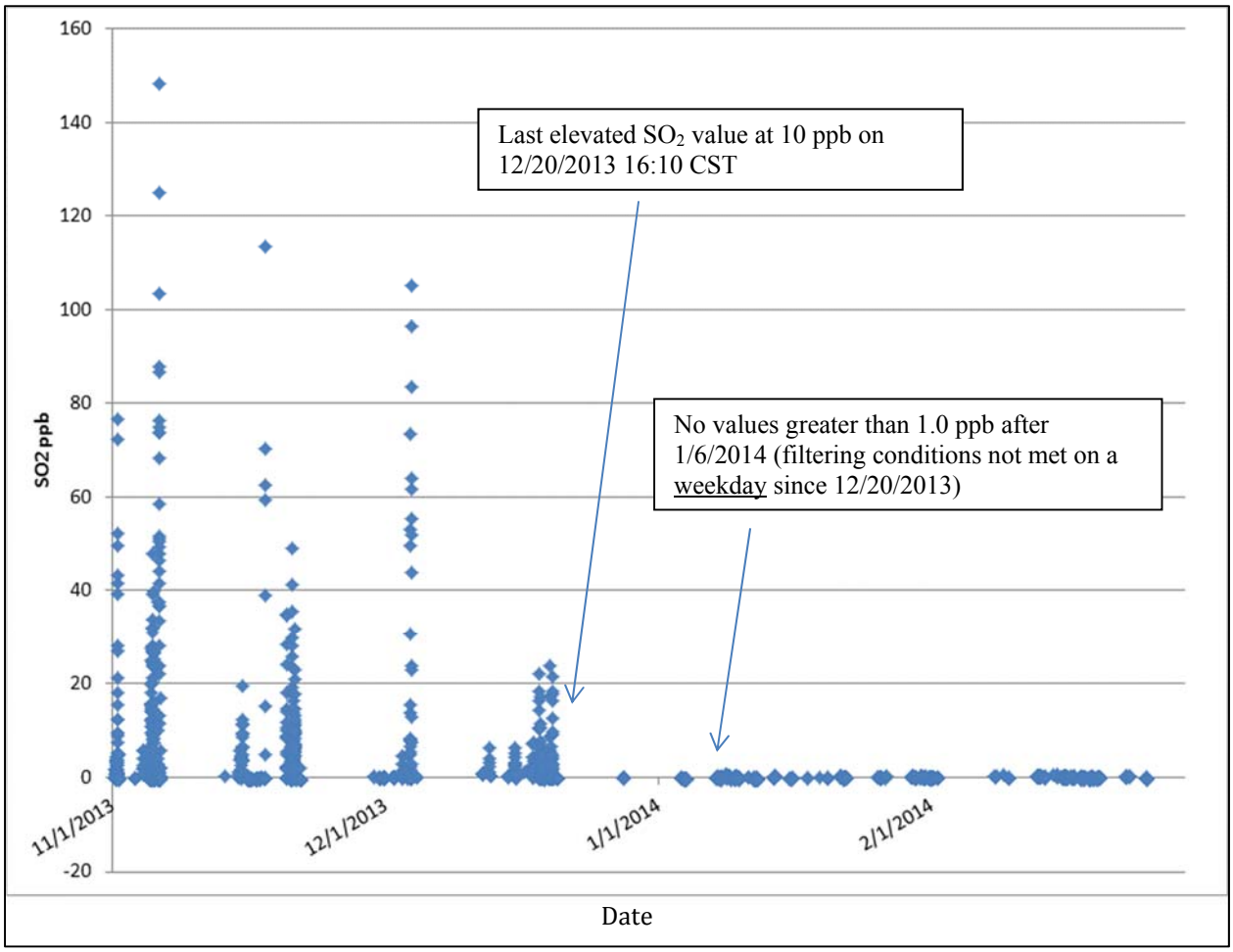
- When the wind blew from the refinery areas, the nearby FHR Easement CAMS 632 site measured elevated SO_2, and when winds blew from the direction of the suspect source, the CAMS 632 site <u>did measure</u> elevated SO_2. CAMS 632 housed a Thermo 43C SO_2 monitor.

This led to the hypothesis <u>that the different models of monitors (API 100A, Thermo-43C, ML-9850) all correctly measured SO_2</u>, and <u>that the two Project sites measured some other chemical or chemicals in the air emitted from the suspect source facility that caused different levels of response in the different models of SO_2 monitors</u>. In addition, since none of the three models at Tuloso CAMS 21 measured SO_2 from the direction of the suspect source facility, then an additional hypothesis was that <u>deposition or reactions occurred in the air between Solar Estates and Tuloso so emissions from the suspect source were not measureable at Tuloso</u>.

UT Austin staff did discuss possible efforts to determine what the interferent was that affected the project sites. However, before any decisions were made, at the end of 2013 the detection of

SO_2 under southeast winds at Solar Estates ended. The last elevated SO_2 measurement under southeast winds was made on Friday December 20, 2013, at 16:10 CST, after which winds did not arrive from the southeast during weekday business hours again until Wednesday January 6, 2014. See Figure 3-108, below. Thus, sometime in this two and half week period the emissions of the interferent ended.

Figure 3-108. Solar Estates CAMS 633 sulfur dioxide (SO_2) concentrations at the 5-minute time scale resolution, wind directions between 140 and 170 degrees, between 4 CST and 20 CST, November 2013 - February 2014



3.5.6 Oak Park CAMS 634

Oak Park CAMS 634 Site Characteristics

The Oak Park site was located at 842 Erwin St, Corpus Christi, TX 78408, at latitude 27º 47' 56" North (27.7989º), longitude -97º 26' 2" West (-97.4339 º), and elevation 12.0 m. The site was recorded with the EPA site number 483550035, and TCEQ CAMS number 634. It was activated on December 2, 2004, and began producing data in mid-December. The site was decommissioned on May 22, 2016.

An aerial image of the site appears in Figure 3-109, below. The site was within a single family neighborhood adjacent to a small park. Figure 3-110, page 3-83, shows a higher altitude aerial image showing the Oak Park site along with three TCEQ sites nearby and their positions relative to major industrial facilities and residential areas.

Based on a low average wind speed of approximately 6 mph, the site is not as well exposed as some other Corpus Christi sites. Figure 3-111, page 3-83, shows a histogram of the wind directions measured over 11.5 years at Oak Park, and Figure 3-112, page 3-84, shows a histogram of the wind speeds.

Figure 3-109. Oak Park CAMS 634 aerial view from 250 m

Figure 3-110. Oak Park, and TCEQ CAMS sites – Palm, Williams Park, Huisache, Hillcrest – 4 km aerial view

Figure 3-111. Oak Park CAMS 634 wind direction distribution

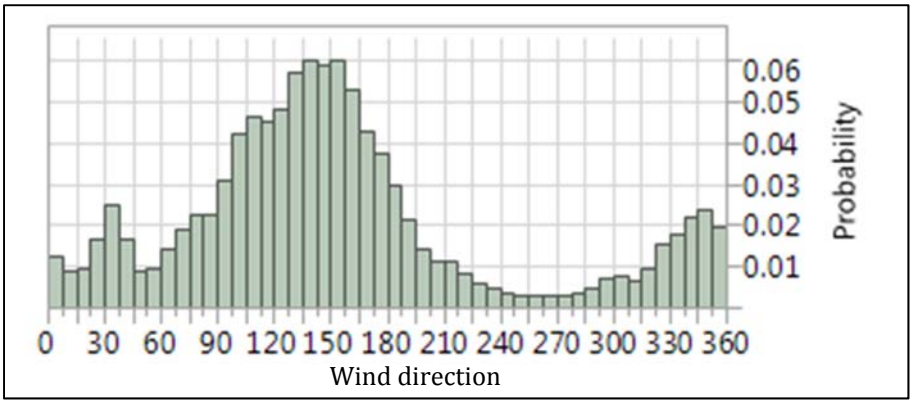
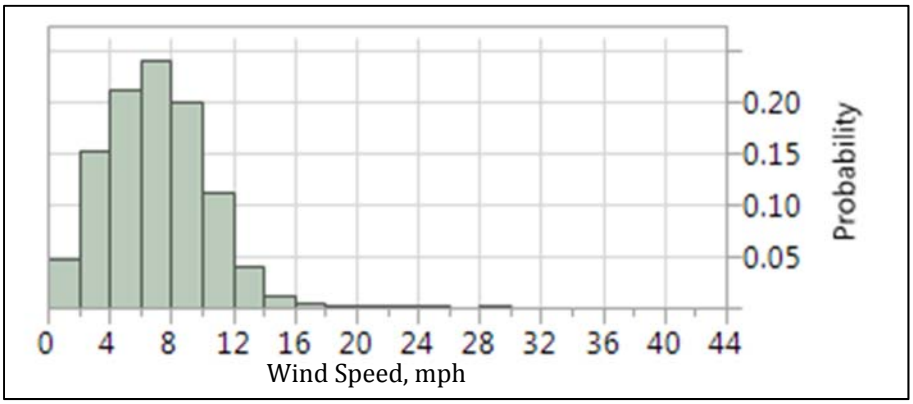


Figure 3-112. Oak Park C634 wind speed distribution



Oak Park CAMS 634 TNMHC

Figure 3-113, page 3-85, shows the time series for hourly TNMHC measurements from the Oak Park site, which ended measuring TNMHC in 2012. Figure 3-114, page 3-85, shows the time series for the mean TNMHC concentration by quarter of the year. Concentrations declined continuously and presented a relatively stable seasonal pattern until instrument decommissioning.

Figure 3-115, page 3-86, is a CPF contour plot of the frequency with which a TNMHC concentration exceeds the 95th percentile 5-minute value of 460 ppbC over the period of monitoring. The image is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows that the upper 5-percentile highest concentrations came from northeast, and the frequency declined by 2008, with another emission source to the northwest, that seemed to persist up until 2012 just short of the instrument decommissioning.

Figure 3-113. Time series for hourly TNMHC concentrations, ppbC units, Oak Park CAMS 634 site

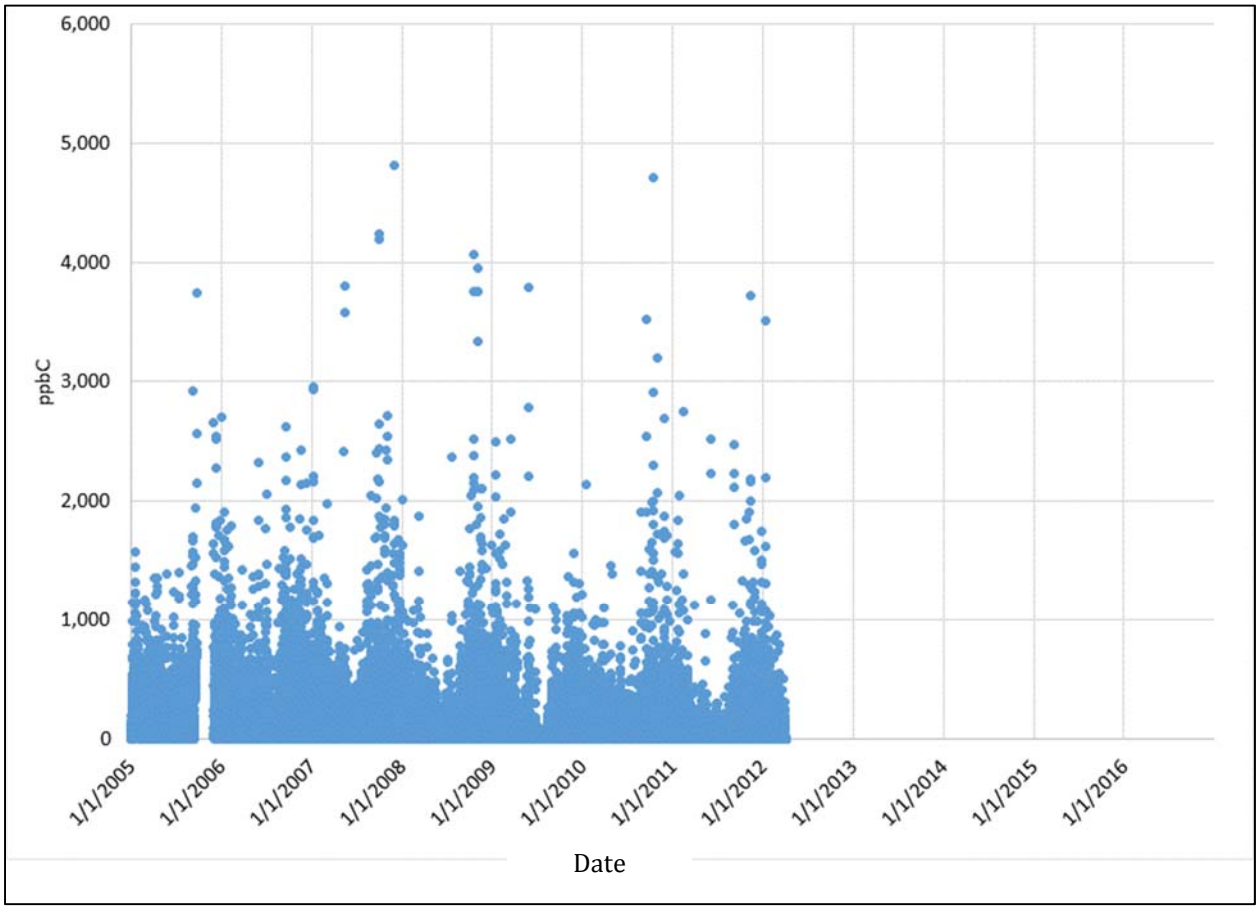


Figure 3-114. Oak Park CAMS 634 TNMHC quarterly mean concentrations, Jan. 2005 – May 2012

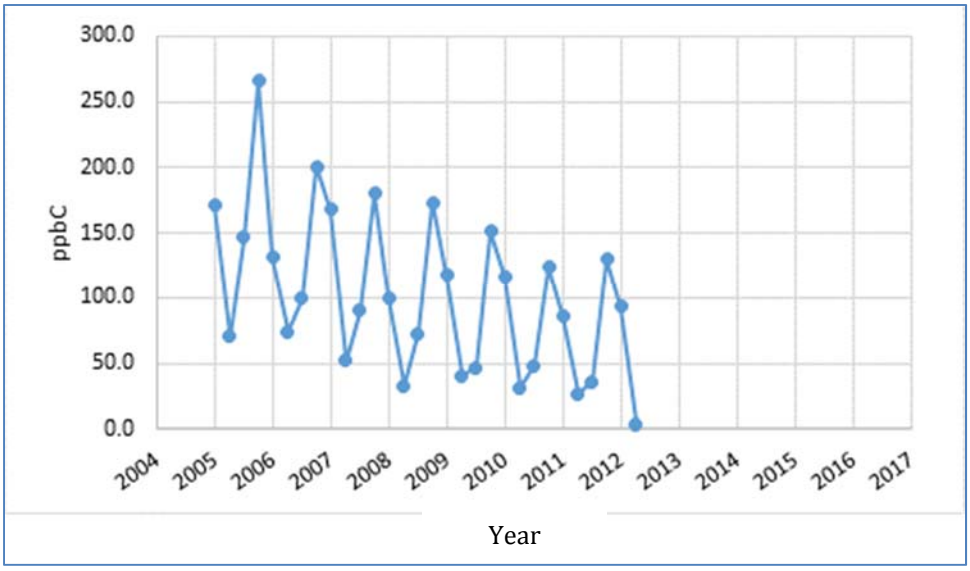
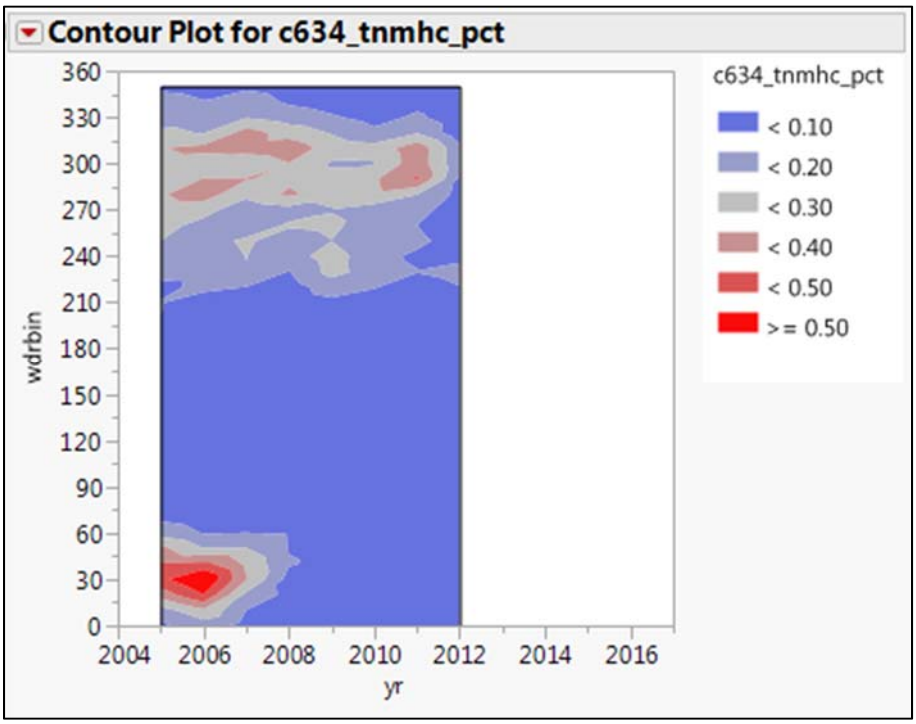


Figure 3-115. Contour plot of frequency that TNMHC concentrations exceeded the 95th percentile 5-minute value for TNMHC at Oak Park CAMS 634



Oak Park Auto-GC data

The quarterly average trends for alkane species from the Oak Park auto-GC are shown in Figure 3-116, page 3-88. The graph looks very similar to the same species graph in Figure 3-86, page 3-68, for the Solar Estates auto-GC. Like Solar Estates, from 2005 to 2011, mean concentrations at Oak Park for all alkanes had a downward trend. However, from 2011 to 2015 the alkane mean concentrations for ethane, propane, and several other species increased during the first and fourth quarters, with a decrease in the fourth quarter of 2015 and first quarter of 2016.

Benzene, ethylbenzene, toluene, and xylene-isomers are grouped as BTEX compounds and shown in Figure 3-117, page 3-89. These species have had a downward trend, flattening out in recent years. Unlike the alkanes, the BTEX species were generally higher in concentration at Oak Park than Solar Estates (compare to Figure 3-87, page 3-69).

Figure 3-118, page 3-90, shows the quarterly means for alkene species. These species have had a downward trend, flattening out in recent years. Again, unlike the alkanes, the alkene species were generally higher in concentration at Oak Park than Solar Estates (compare to Figure 3-88, page 3-70).

The heavy nine to ten carbon species are shown in Figure 3-119, page 3-91. These species have shown a downward trend over time and were roughly comparable to Solar Estates (compare Figure 3-89, page 3-71). However, during the month of April 2012, the Oak Park site measured elevated concentrations of isopropyl-benzene, also known as cumene, an odorous compound. This is discussed in a case study later in this chapter.

As was noted earlier in this report, two species of particular concern for toxicological matters are benzene and 1,3-butadiene, two hydrocarbons measured by the Project auto-GCs and canister sample analyses. Figure 3-120, page 3-92, shows the time series for benzene at the Oak Park site from the start of instrument operation on March 1, 2005, to the end of operation on May 21, 2016. Concentrations are in ppbV, which are used for toxicological evaluation. The short term AMCV for benzene is 180 ppbV and the maximum one hour concentrations at Oak Park was 120 ppbV taken on January 27, 2007, at 6:00 CST. And the second highest one-hour concentration was 86 ppbV on November 6, 2009, at 4 CST. These two points are statistical outliers and Figure 3-121, page 3-93, shows the Oak Park benzene data sans these two points. The long term AMCV for benzene is 1.4 ppbV and the average concentration over the duration of the project was 0.42 ppbV.

Figure 3-122, page 3-94, shows the time series for 1,3-butadiene at Oak Park. Concentrations are in ppbV, which are used for toxicological evaluation. The short term AMCV for 1,3-butadiene is 1,700 ppbV and the maximum one hour concentrations at Oak Park was 15.5 ppbV taken on October 17, 2010, at 8:00 CST. The long term AMCV for 1,3-butadiene is 9.1 ppbV and the average concentration over the duration of the project was 0.04 ppbV.

Figure 3-116. Oak Park CAMS 634 auto-GC alkane species quarterly means March 2005 – May 2016

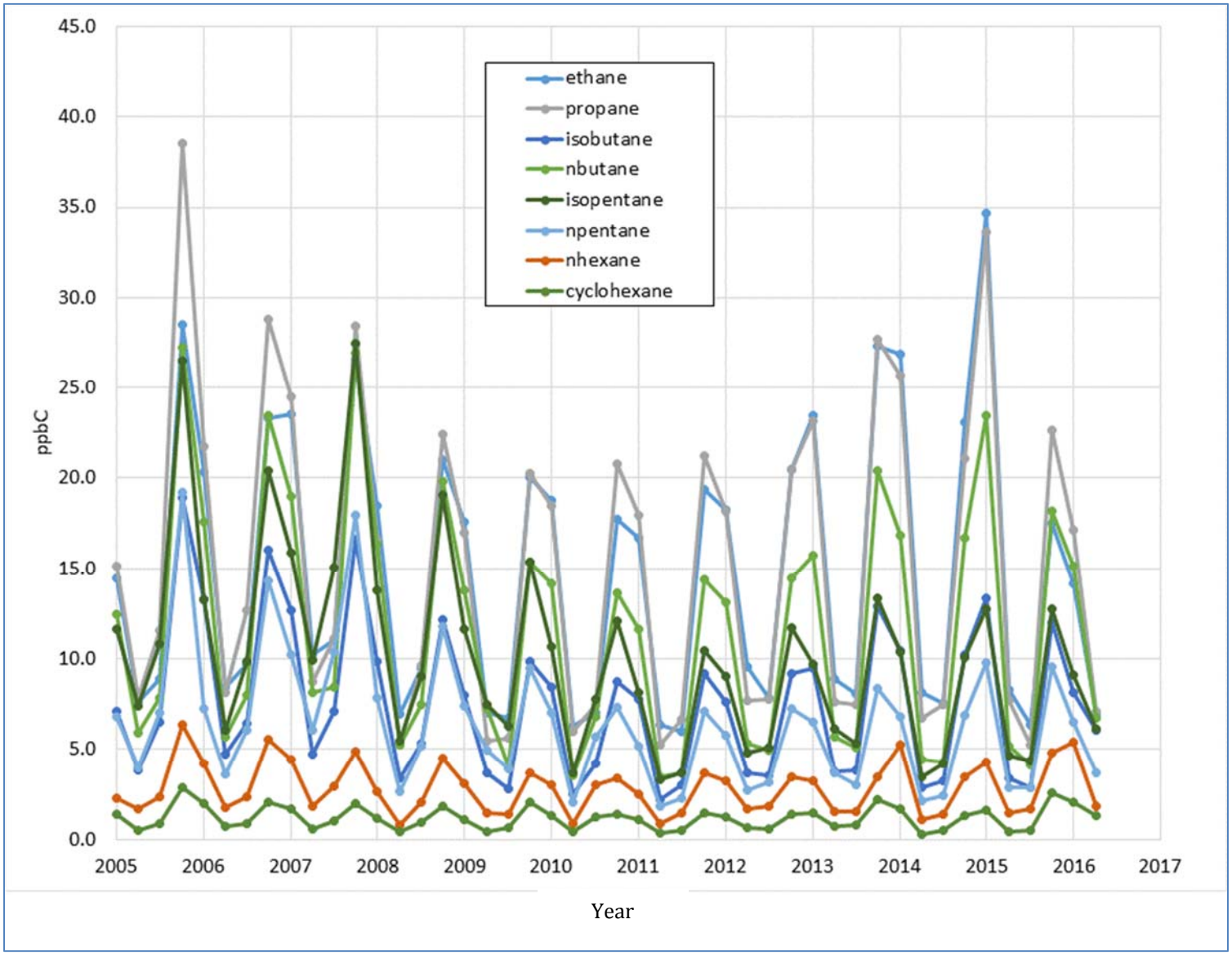


Figure 3-117. Oak Park CAMS 634 auto-GC BTEX species quarterly means March 2005 – May 2016

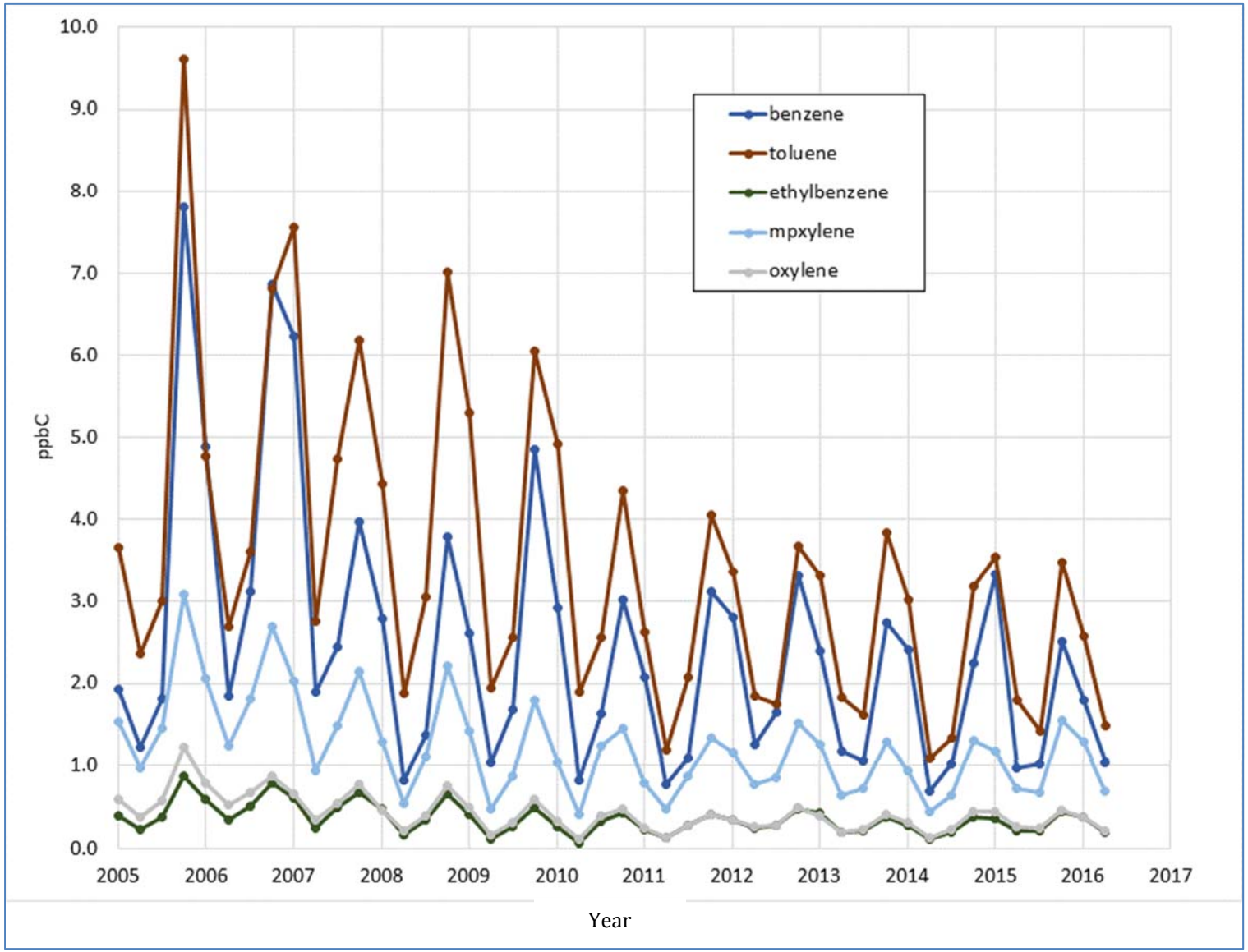


Figure 3-118. Oak Park CAMS 634 auto-GC alkene species quarterly means March 2005 – May 2016

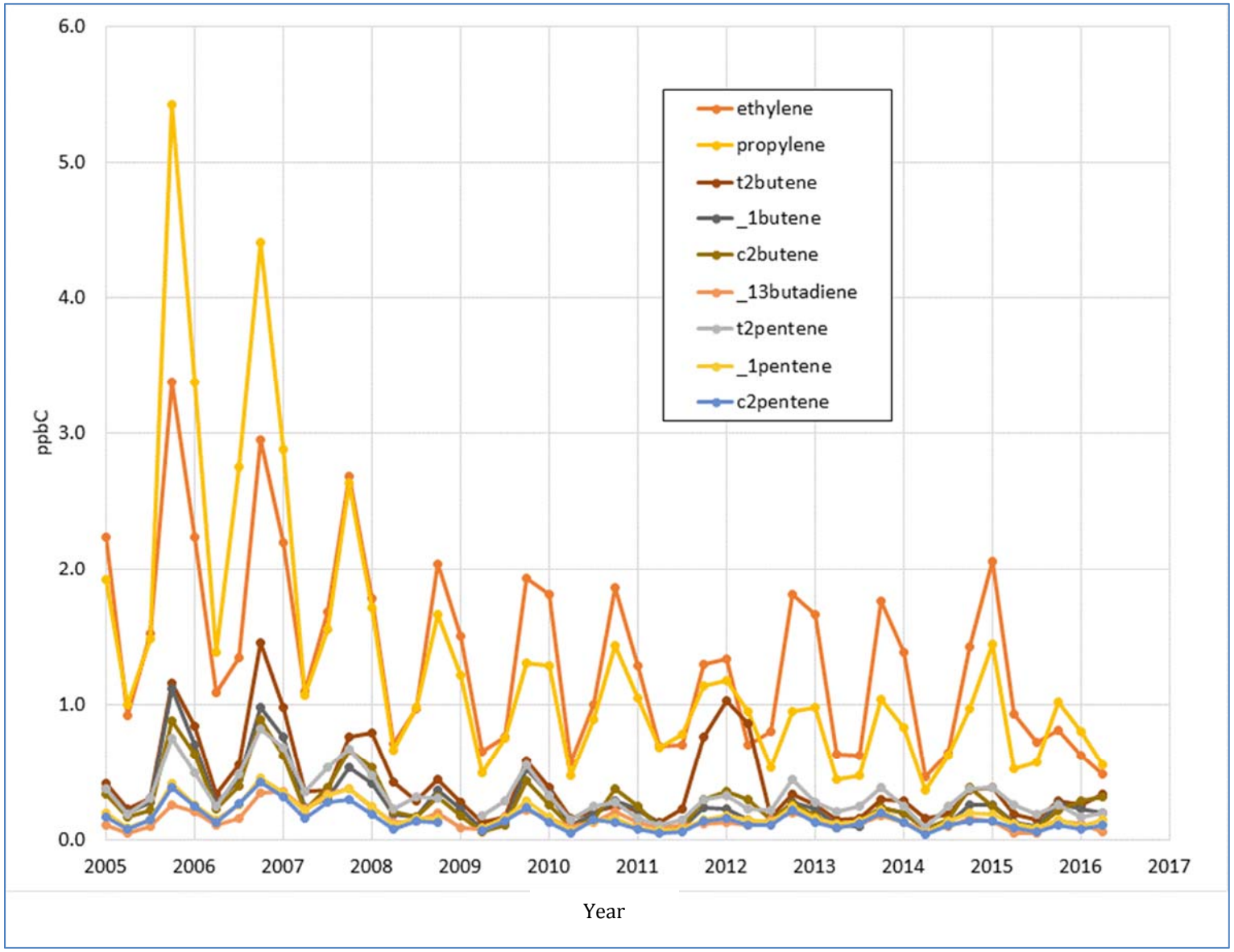


Figure 3-119. Oak Park CAMS 634 auto-GC C9 – C10 species quarterly means March 2005 – May 2016

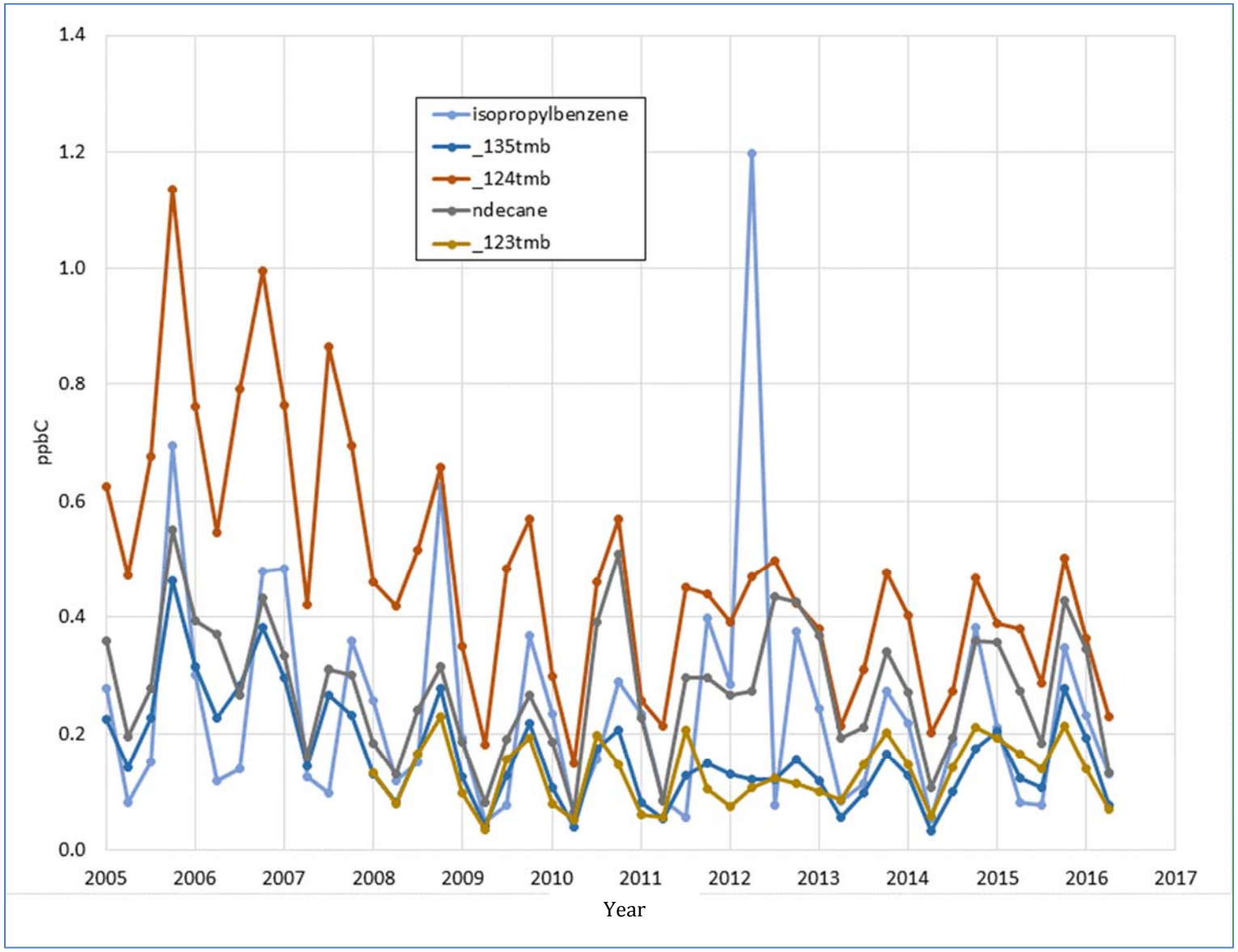


Figure 3-120. Oak Park benzene ppbV units, March 1, 2005 - May 21, 2016

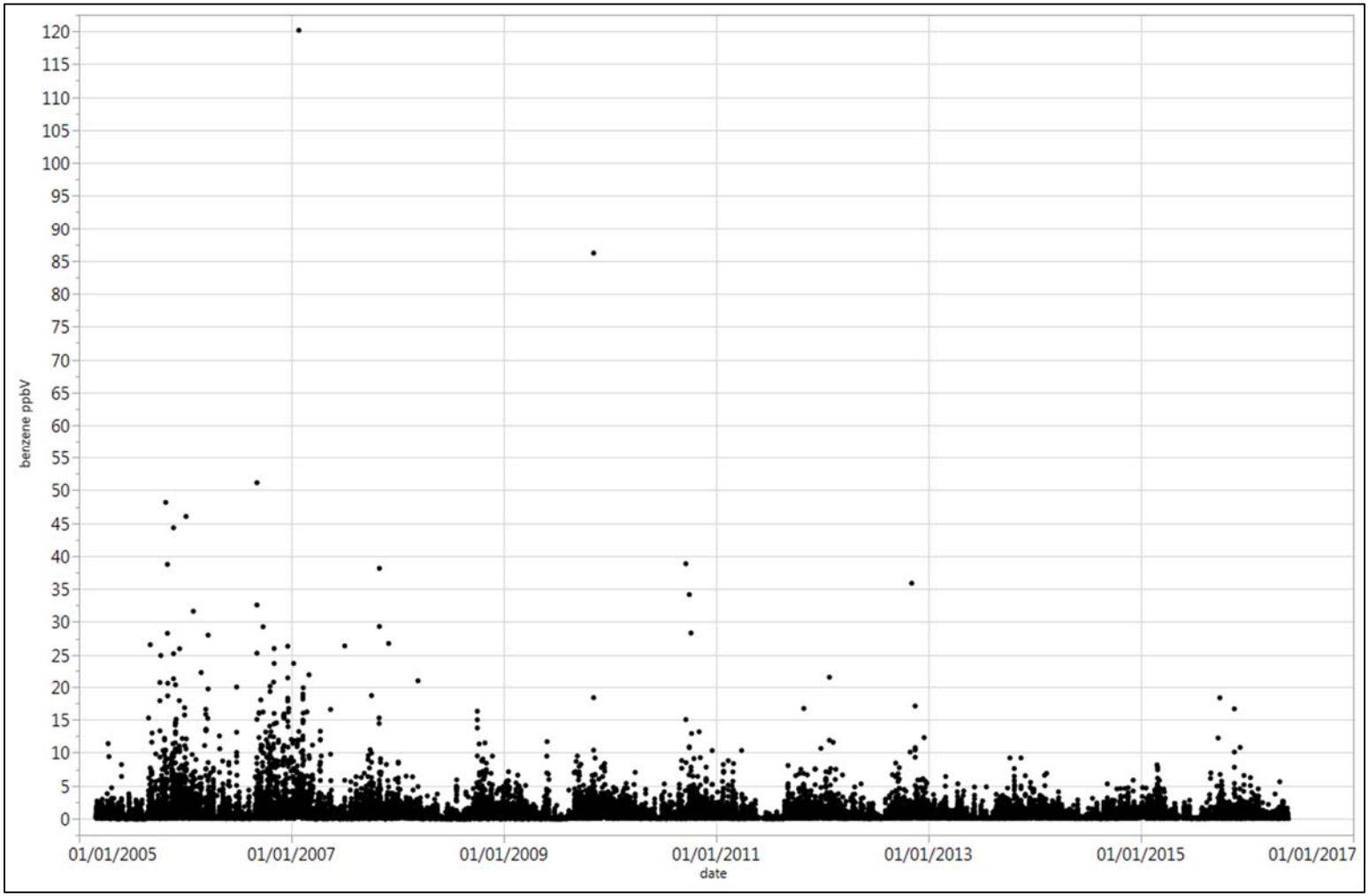


Figure 3-121. Oak Park benzene ppbV, March 1, 2005 – May 21, 2016, 2 outliers excluded

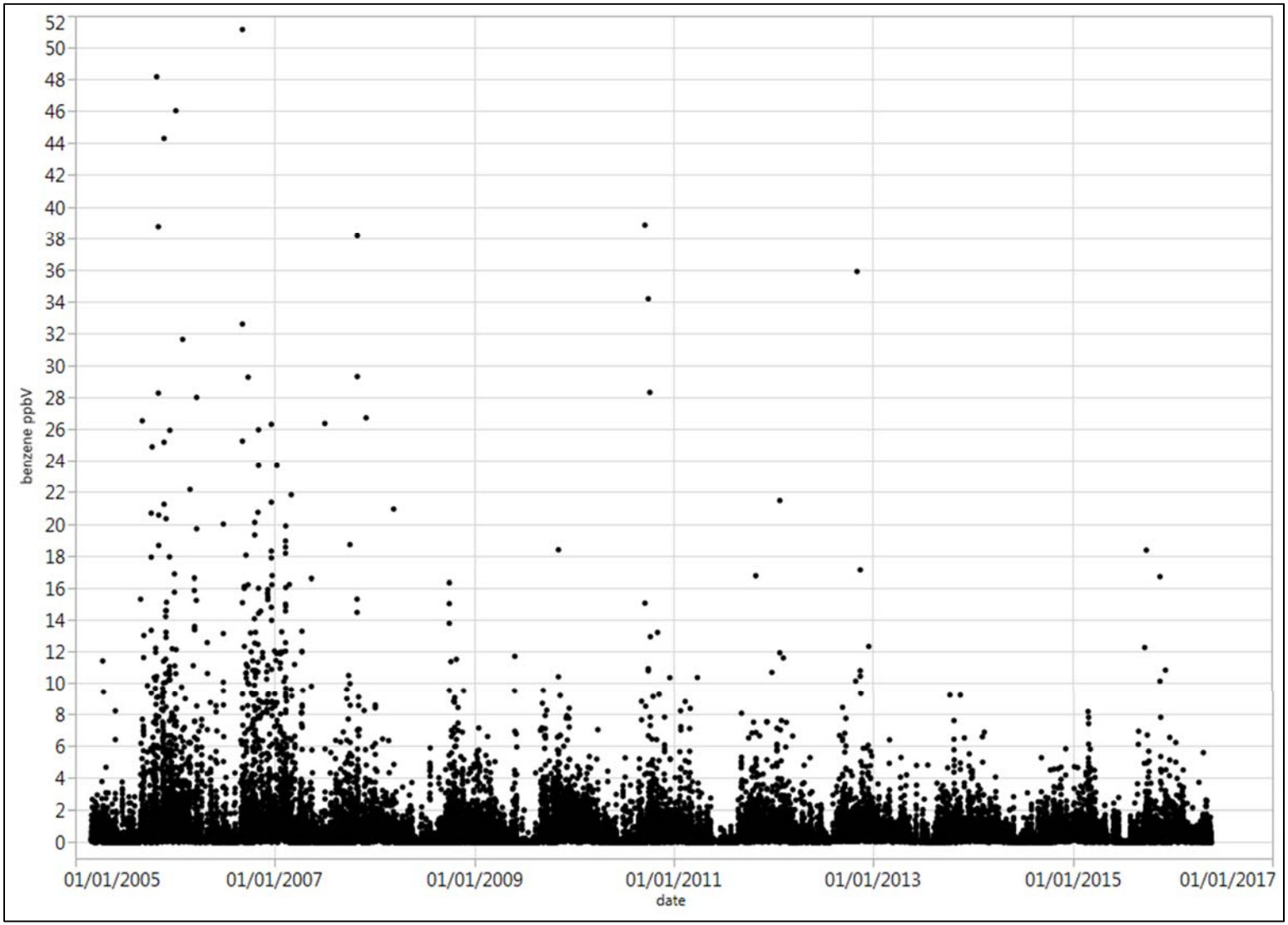
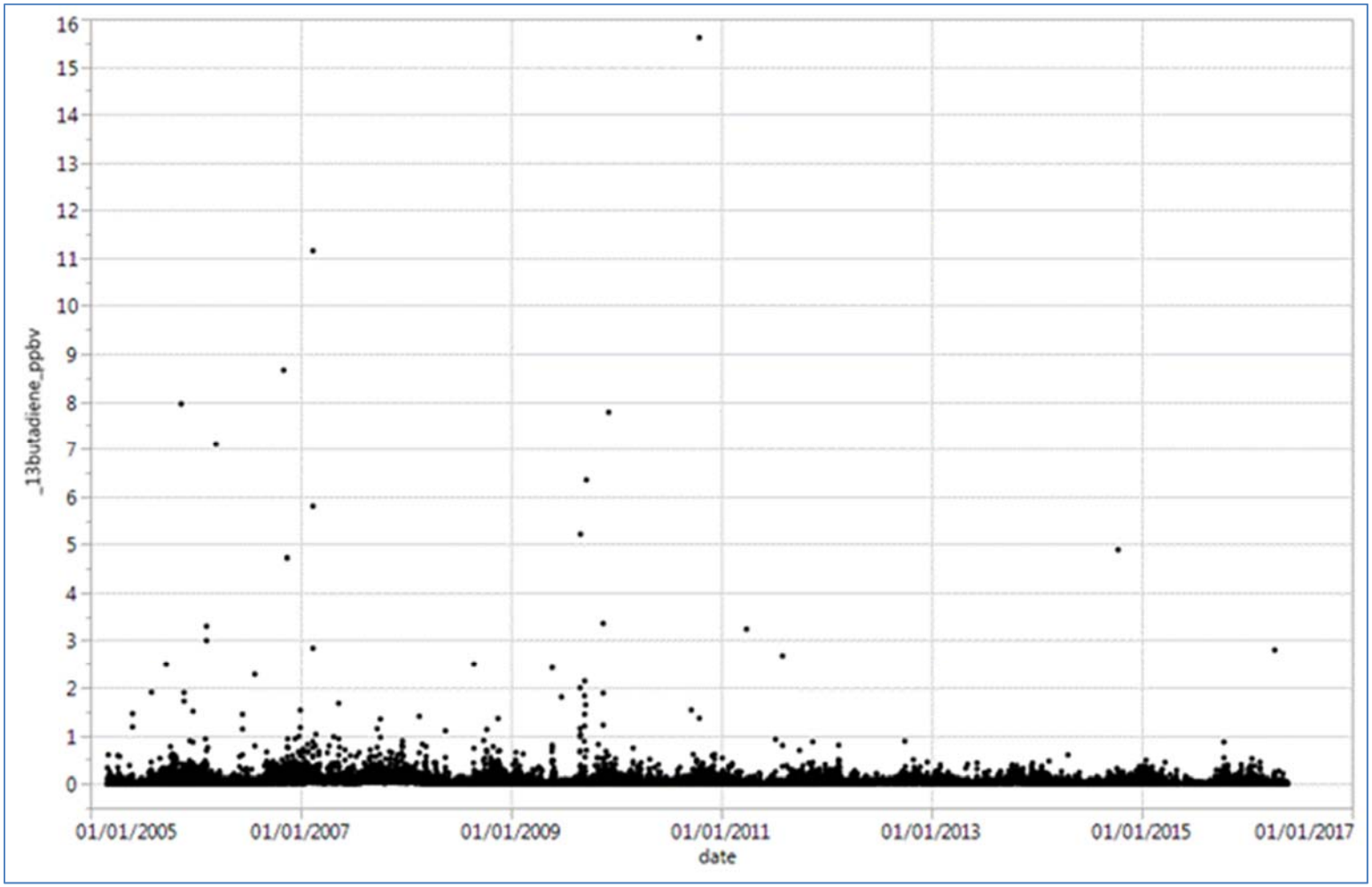


Figure 3-122. Oak Park 1,3-butadiene ppbV, March 1, 2005 – May 21, 2016



Case study on elevated isopropyl-benzene at Oak Park April 2012

As can be noted in the graph in Figure 3-119, page 3-91, for nine to ten carbon species quarterly concentrations over time, there is an apparent outlier quarter for isopropyl-benzene in the second quarter of 2012. Figure 3-123, below, shows a time series graph for the nine to ten carbon species hydrocarbons at Oak Park from March 1 to June 30, 2012. In Figure 3-124 page 3-96, the isopropyl-benzene concentrations have been averaged by 5 degree wind bins for all wind directions except westerly, which are given wider 20 degree bins owing to the relatively fewer winds from that range of directions. The highest concentrations were associated with winds from 35 – 40 degrees bearing from Oak Park. Figures 3-125 to 3-128, pages 3-96 to 3-98, show surface back trajectories associated with individual elevated isopropyl-benzene values on four different days in April 2012 that all look similar and track to the northeast in concurrence with the directionality in Figure 3-124. Figure 3-129, page 3-98, shows an areal image of Oak Park with a ray drawn at a bearing of 37.5 degrees from the site, that passes over a refinery northeast of the site.

Figure 3-123. Time series for heavier hydrocarbons at Oak Park March - June 2012

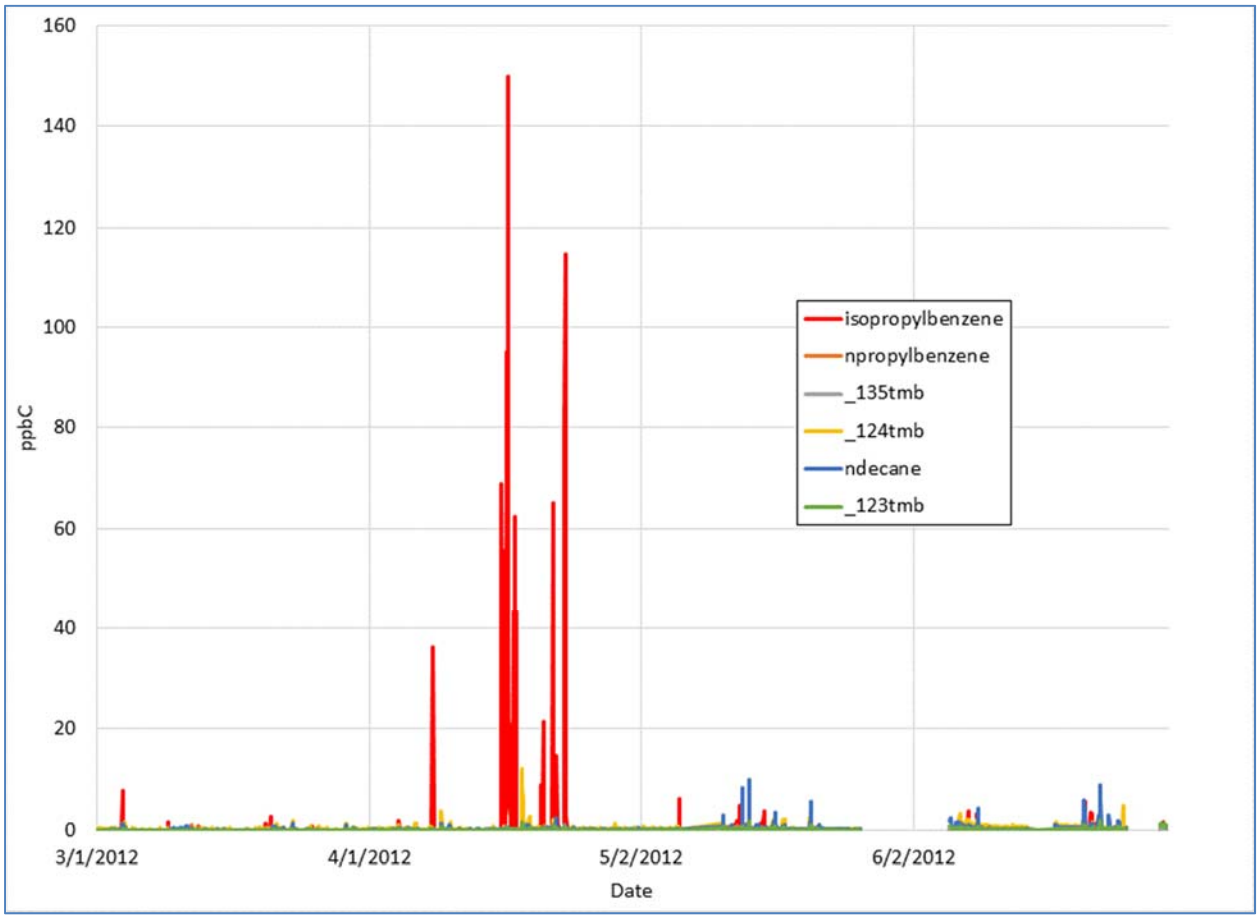


Figure 3-124. Oak Park mean isopropylbenzene concentration ppbC by wind direction April 2012

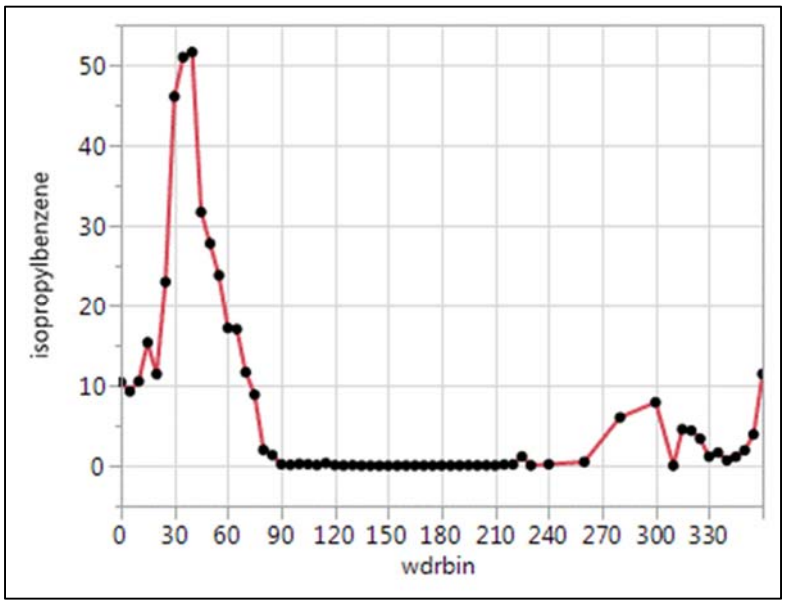


Figure 3-125. Surface back-trajectory from Oak Park CAMS 634 at 20:20 CST 4/16/2012

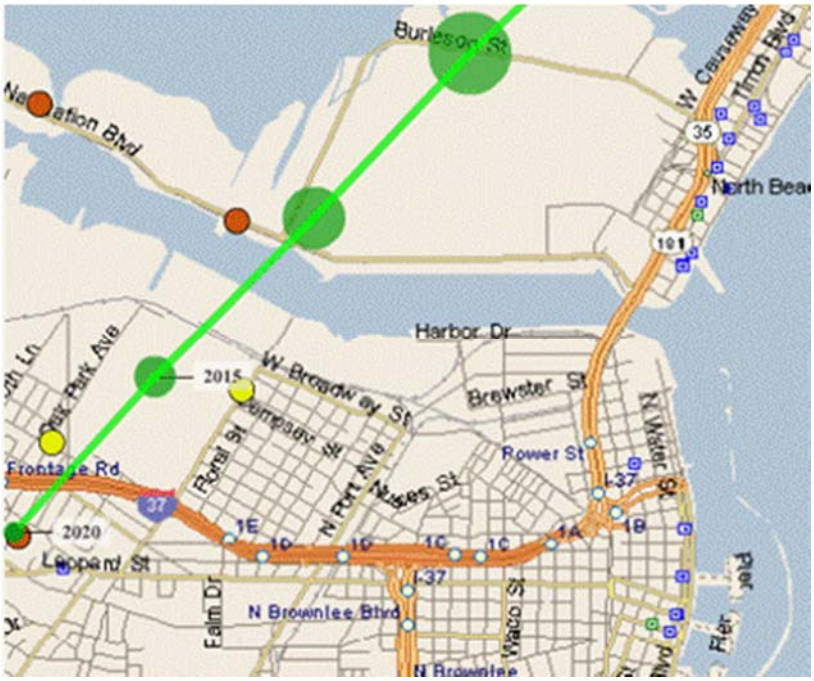


Figure 3-126. Surface back-trajectory from Oak Park CAMS 634 at 15:20 CST 4/17/2012

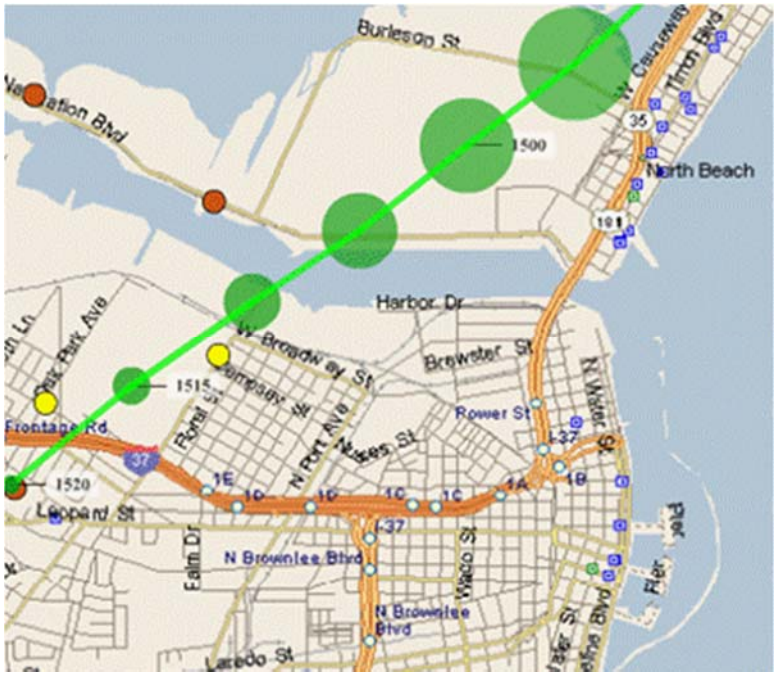


Figure 3-127. Surface back-trajectory from Oak Park CAMS 634 at 7:20 CST 4/23/2012

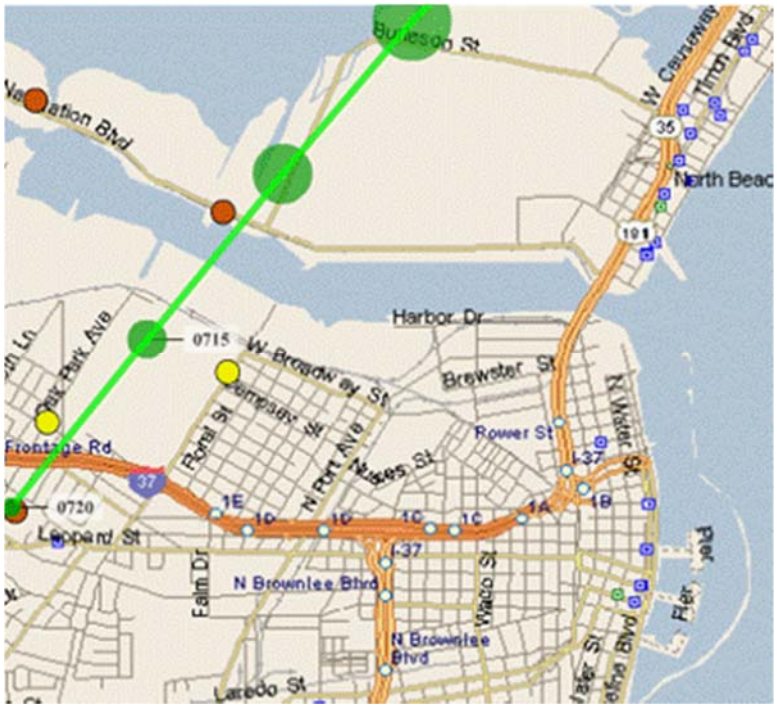


Figure 3-128. Surface back-trajectory from Oak Park CAMS 634 at 11:20 CST 4/21/2012

Figure 3-129. Aerial of Oak Park with ray drawn at 37.5 degrees

3.5.7 Dona Park CAMS 635

Dona Park CAMS 635 characteristics

The Dona Park site was located at 5707 Up River Rd, Corpus Christi, TX 78407, at latitude 27º 48' 43" North (27.8118º), longitude -97º 27' 57" West (-97.4657 º), and elevation 6.0 m. The site was recorded with the EPA site number 483550034, and TCEQ CAMS number 635. The UT equipment began producing data in mid-December 2004. The site was partially decommissioned on May 22, 2016, and SO_2 and H_2S and meteorological monitoring will continue at the site under a contract with the TCEQ. The Project site is collocated with TCEQ site CAMS 199, at which the TCEQ measures particulate matter, meteorology, and samples the air with canisters for 24-hours every 6th day. The TCEQ site has been in operation since 2001.

An aerial image of the site appears in Figure 3-130, below. The site is within a single-family neighborhood adjacent to a small park. Figure 3-131, page 3-100, shows a higher altitude aerial image showing the Dona Park site along with a nearby private company monitoring site, and their positions relative to major industrial facilities, the ship channel, and residential areas.

Based on a low average wind speed ~ 7.6 mph, the site is not as well exposed as some other Corpus Christi sites. Figure 3-132, page 3-100, shows a histogram of the wind directions measured over 11.5 years at Dona Park, and Figure 3-133, page 3-101, shows a histogram of the wind speeds.

Figure 3-130. Dona Park CAMS 635 aerial view

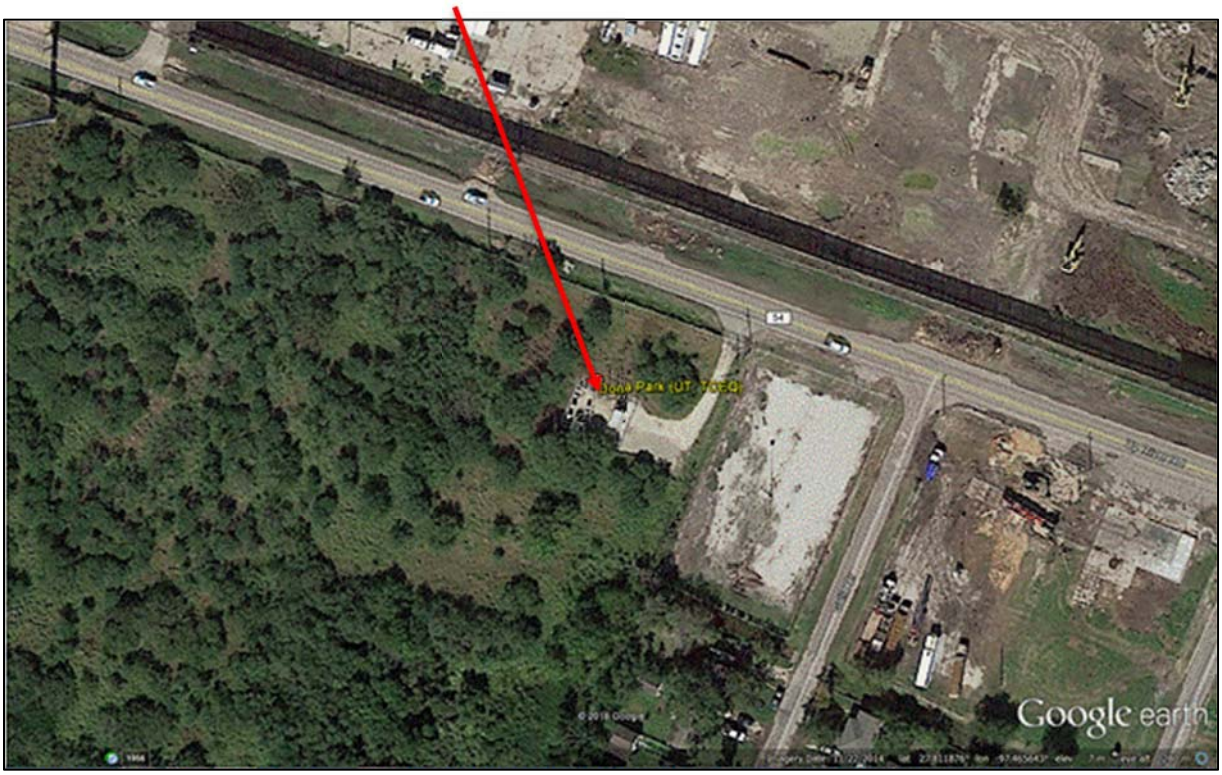


Figure 3-131. Dona Park CAMS 635 aerial view, 4 km altitude

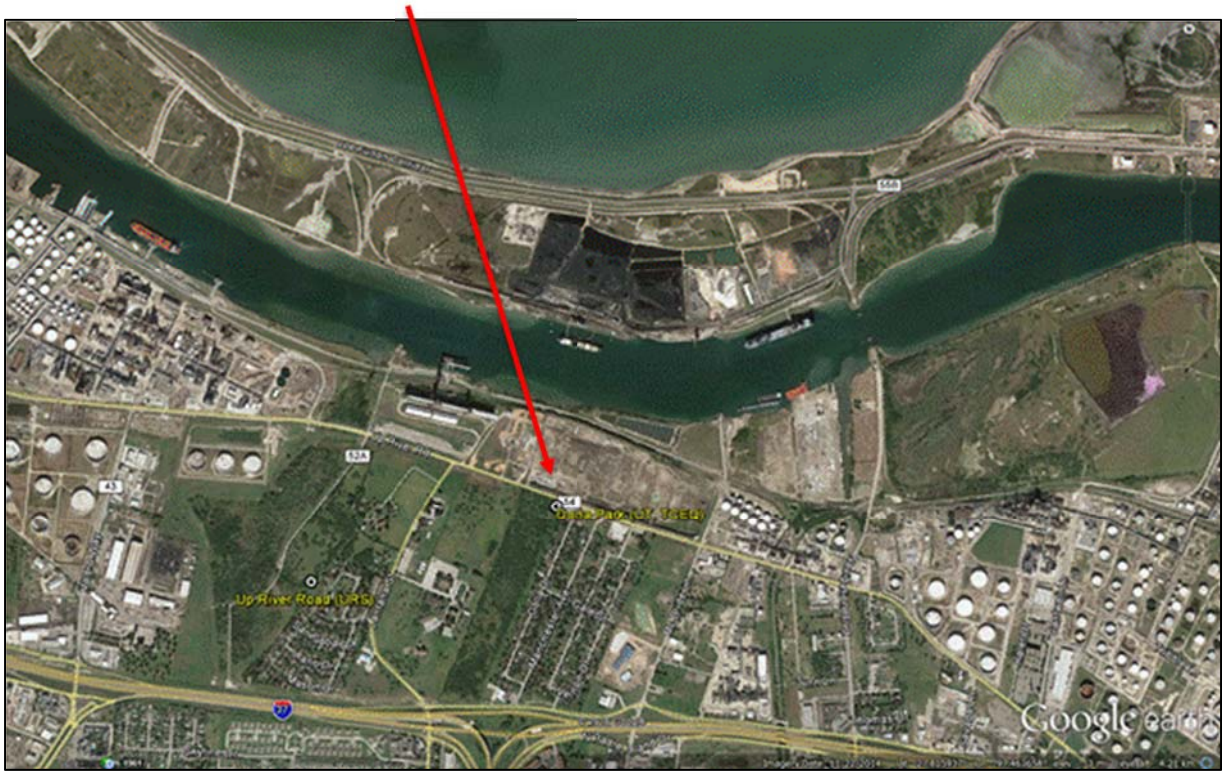


Figure 3-132. Dona Park CAMS 635 wind direction distribution

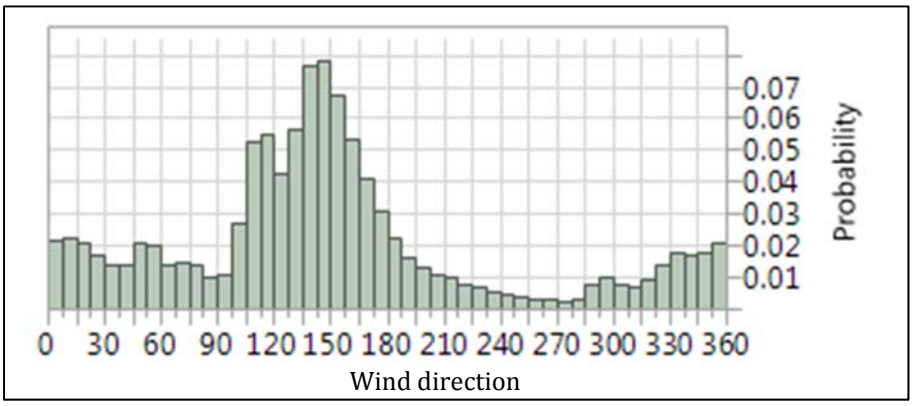
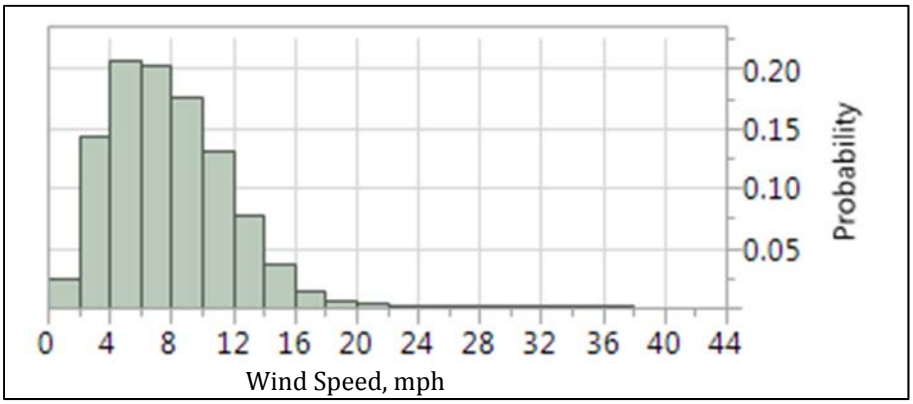


Figure 3-133. Dona Park CAMS 635 wind speed distribution



Dona Park CAMS 635 TNMHC

Figure 3-134, page 3-102, shows the time series for hourly TNMHC measurements from the Dona Park site. Some years appeared to have higher concentration than others, but there was no clear trend. This is confirmed by Figure 3-135, page 3-102, showing the time series for the mean TNMHC concentration by quarter of the year, where again, no trend is clear.

Figure 3-136, page 3-103, is a CPF contour plot of the frequency with which a TNMHC concentration exceeds the 95th percentile 5-minute value of 424 ppbC over the period of monitoring. The image is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows that the upper 5-percentile highest concentrations came from the north and were particularly intense in late 2010 – early 2011.

Figure 3-134. Time series for hourly TNMHC concentrations, ppbC units, Dona Park CAMS 635 site

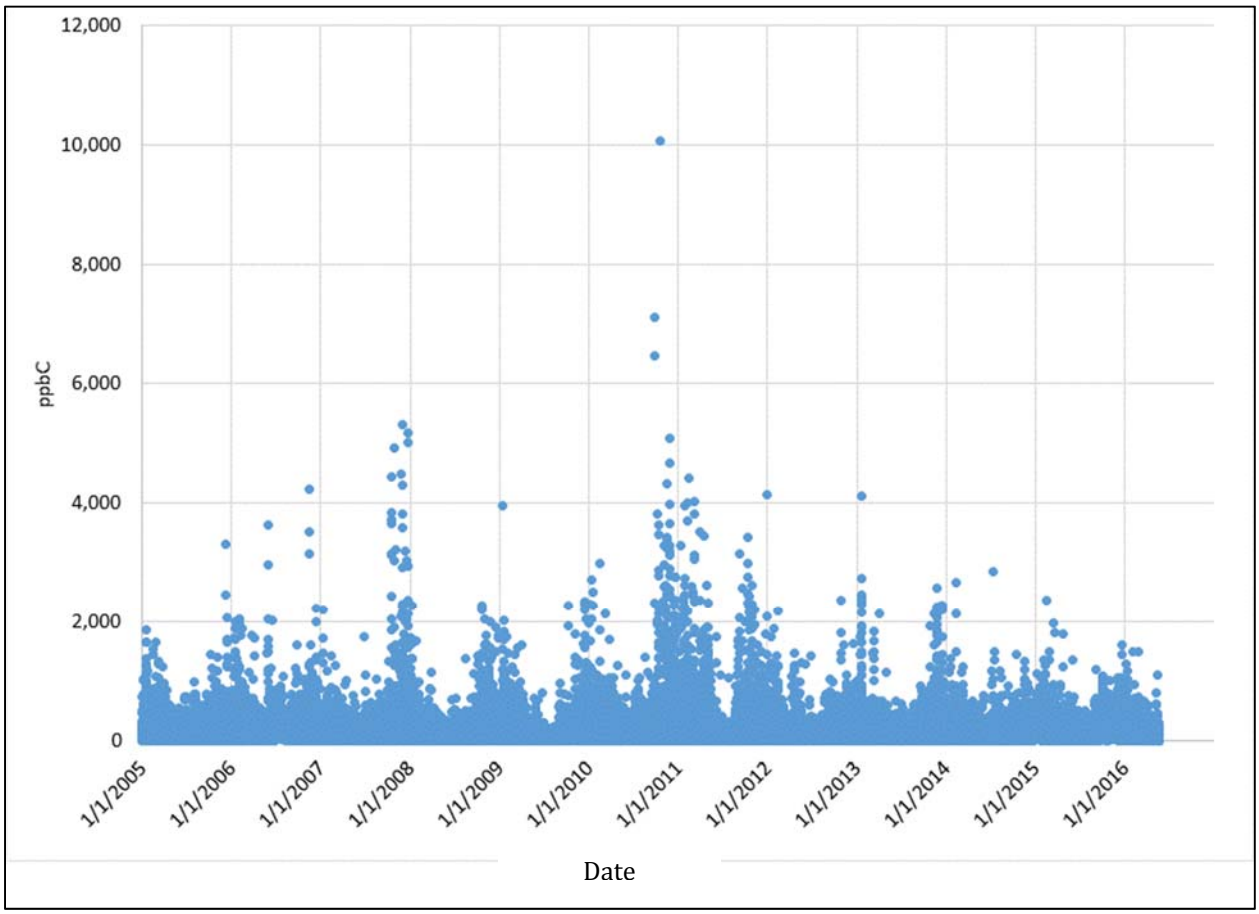


Figure 3-135. Dona Park CAMS 635 TNMHC quarterly mean concentrations, Jan. 2005 – May 2016

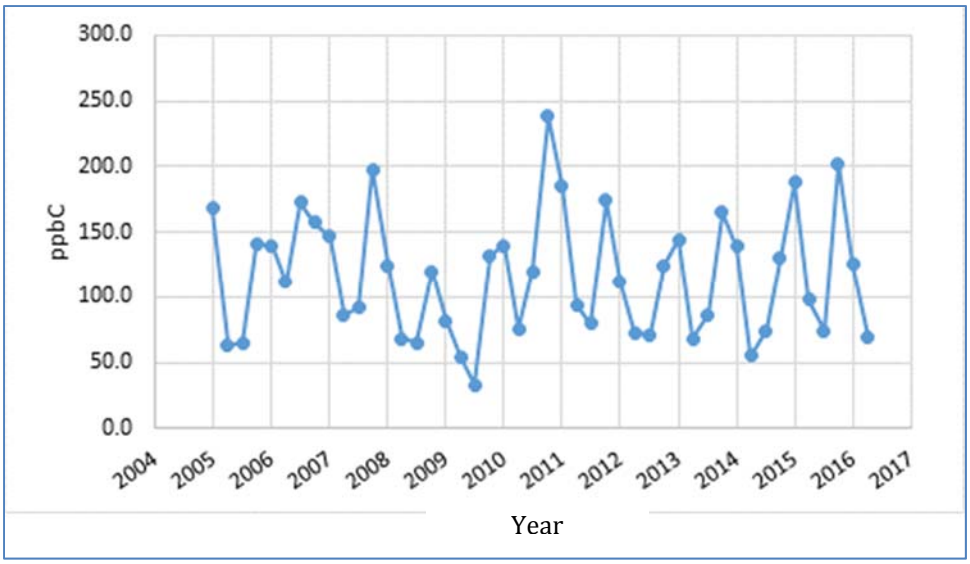
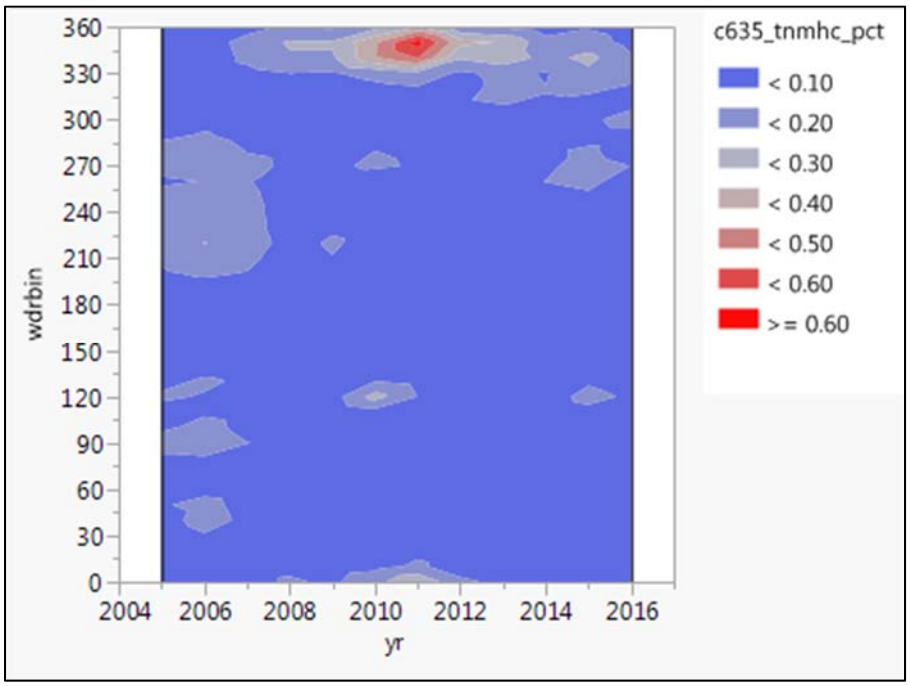


Figure 3-136. Contour plot of frequency that TNMHC concentrations exceeded the 95th percentile 5-minute value for TNMHC at Dona Park CAMS 635 Dona Park



Dona Park CAMS 635 SO_2

As with other sites on this project, the SO_2 concentrations have significantly declined since monitoring began. Figure 3-137, page 3-104, shows the time series for hourly SO_2 measurements. There is very clearly a decrease in the frequency of elevated concentrations over time. Figure 3-138, page 3-104, shows a graph of the mean SO_2 concentration by quarter of the year. Mean concentrations are close to 0.0 ppb in recent years.

Figure 3-139, page 3-105, is a CPF contour plot of the frequency with which an SO_2 concentration exceeds the 95th percentile 5-minute value over the period of monitoring. At Dona Park, only 5 percent of all 5-minute time scale SO_2 measurements were greater than 1.6 ppb. The image in Figure 3-139 is color-coded for the highest frequency of exceedances of the 95th percentile. The figure shows two key directions for elevated SO_2, those being east with some effect from east through north, and northwest around 300 degrees. Dona Park's positioning is such that the site could be affected by the SO_2 from ships at docks as well as by industrial sources.

Figure 3-137. Dona Park CAMS 635 SO_2 time series, Jan. 2005 – May 2016

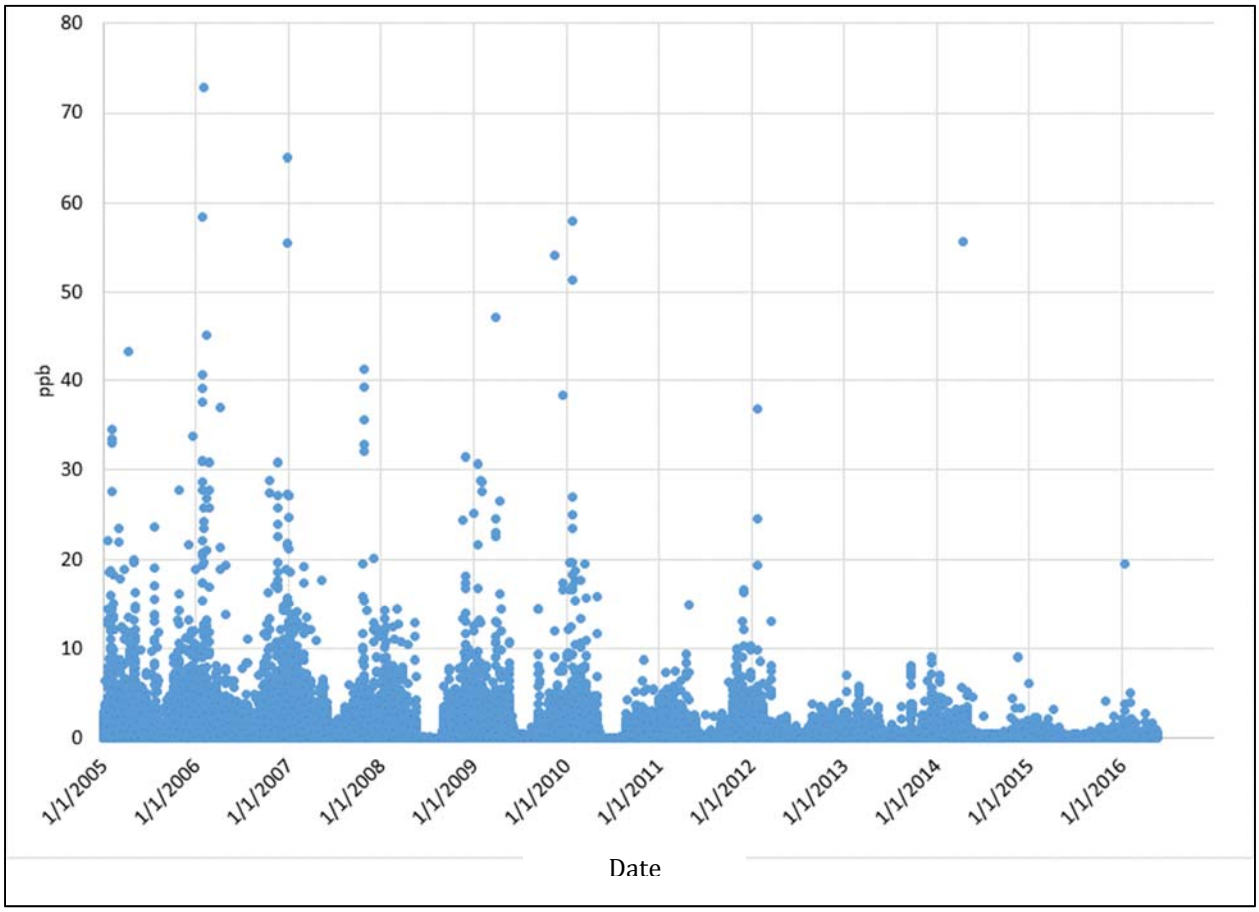


Figure 3-138. Dona Park CAMS 635 SO_2 quarterly mean concentrations, Jan. 2005 – May 2016

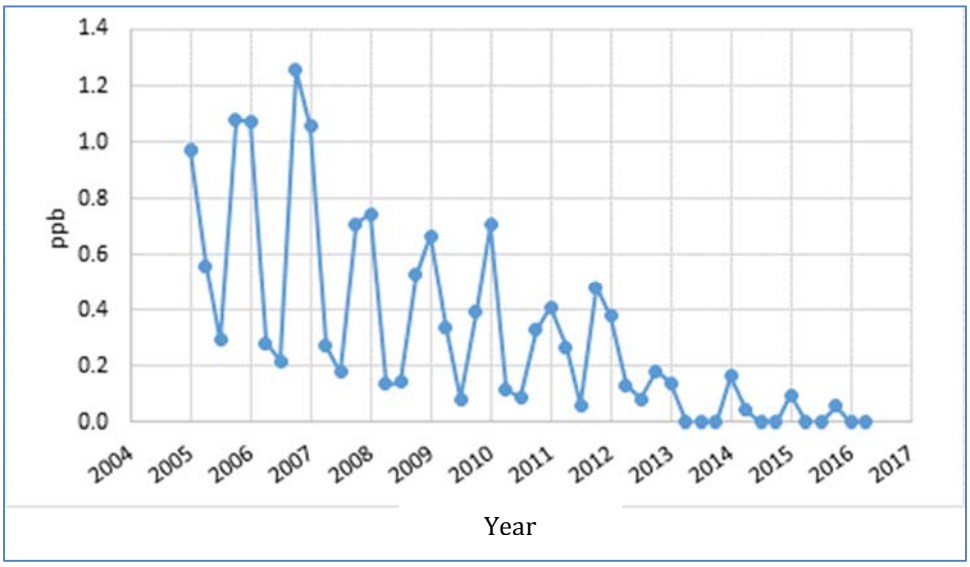
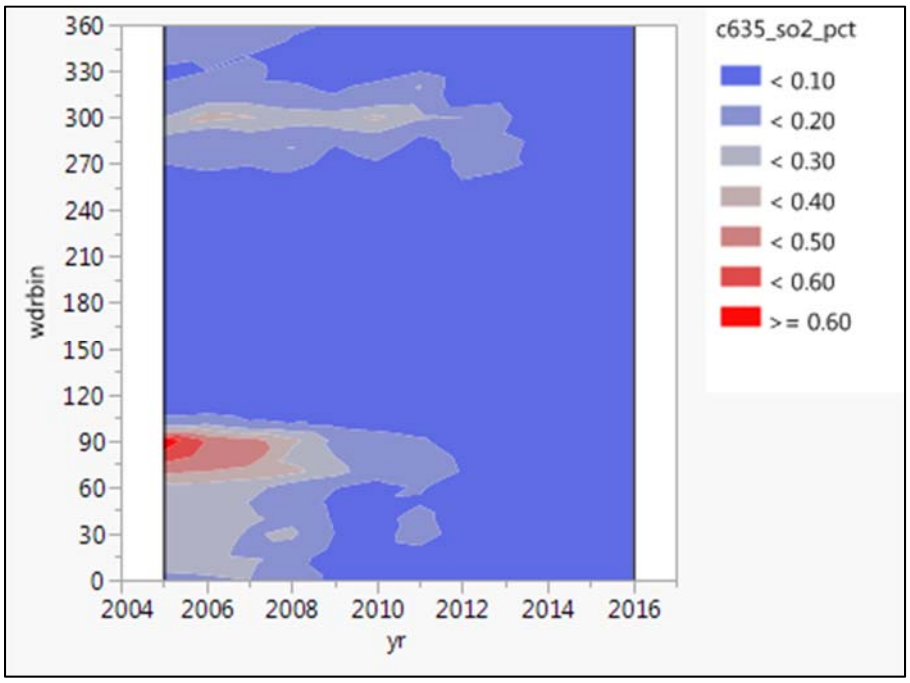


Figure 3-139. Contour plot of frequency that SO_2 concentrations exceeded the 95th percentile 5-minute value for SO_2 at Dona Park CAMS 635



Dona Park CAMS 635 H_2S

Lastly, the third pollutant measured at the Dona Park site has been hydrogen sulfide (H_2S). Concentrations of this pollutant have declined, but not to the near-0.0 background conditions. Figure 3-140, page 3-106, shows the time series for hourly H_2S measurements. Figure 3-141, page 3-106, shows a graph of the mean H_2S concentration by quarter of the year. There is not a clear trend in H_2S.

The CPF contour plot in Figure 3-142, page 3-107, for the wind directions and time periods that H_2S concentration exceeded the 95th percentile 5-minute value of 1.2 ppb over the period of monitoring shows the higher frequency of elevated concentrations in 2006 with some elevated concentrations over the duration of the project from both the west and east.

As was noted earlier, is still being operated by UT Austin under contract with the TCEQ for SO_2, H_2S, and meteorology.

Figure 3-140. Dona Park CAMS 635 H_2S time series, Jan. 2005 – May 2016

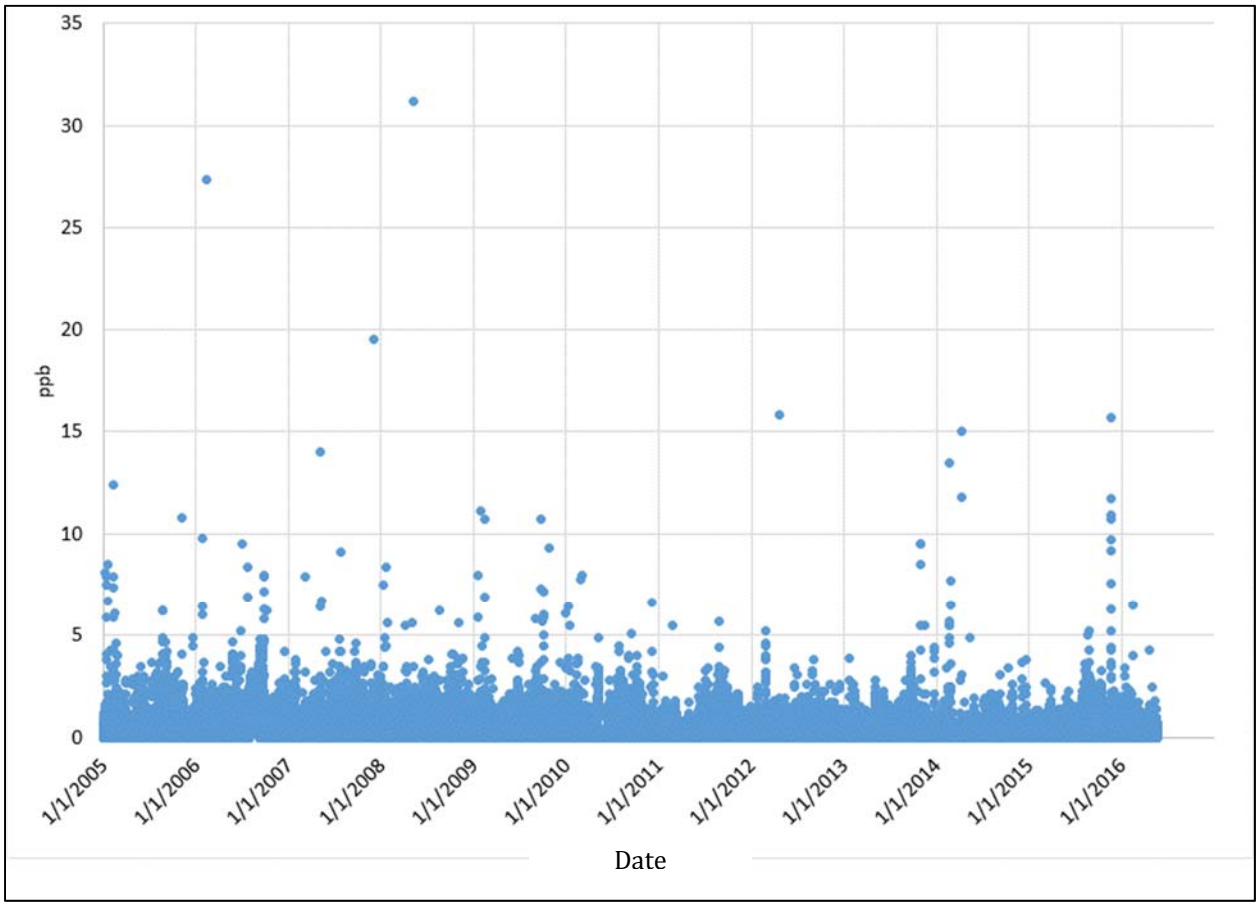


Figure 3-141. Dona Park CAMS 635 H_2S quarterly mean concentrations, Jan. 2005 – May 2016

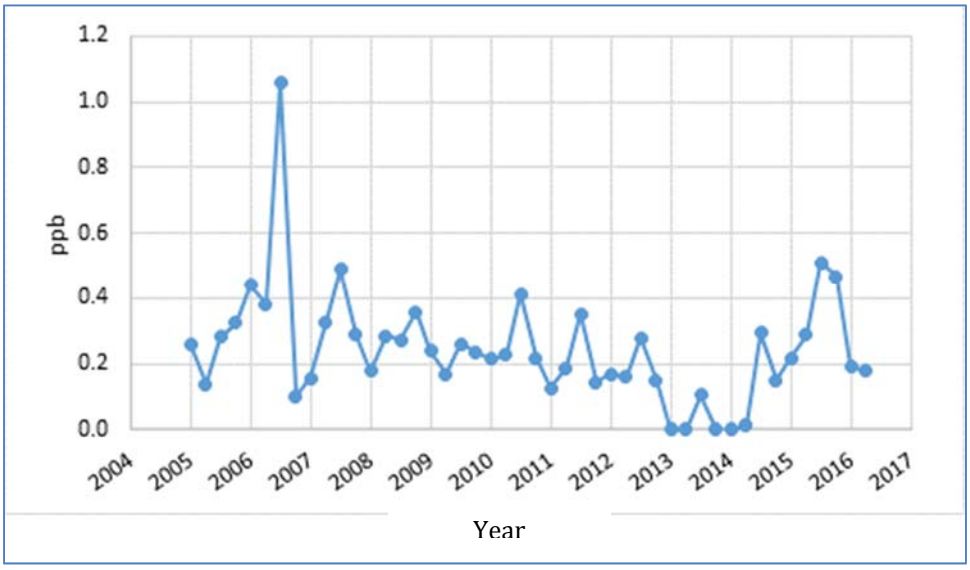
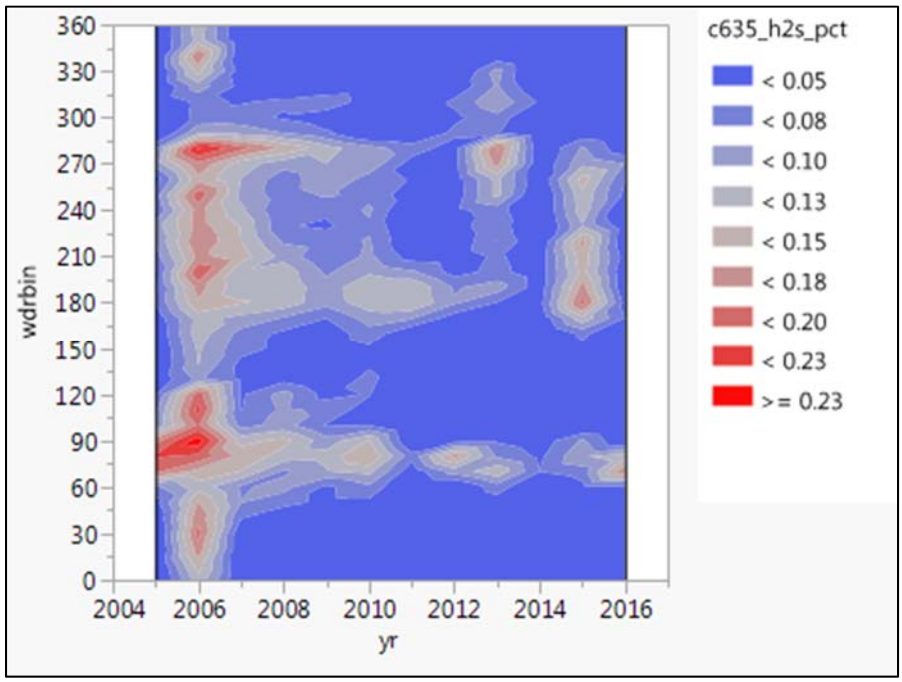


Figure 3-142. Contour plot of frequency that H_2S concentrations exceeded the 95th percentile 5-minute value for H_2S at Dona Park CAMS 635



3.5.8 Use of Data from Different Monitoring Sites to Identify Emission Sources

There were several opportunities, over the course of this project, to use data from two or more monitoring sites to provide evidence as to emission sources. One example was given earlier in the investigation of the interferent at Solar Estates and Flint Hills Resources Easement beginning on page 3-74, where winds from the south southeast at Solar Estates CAMS 633 and winds from the southwest at Flint Hills CAMS 632 both suggested an emission source near the intersection of lines drawn in the peak concentration upwind directions from the two sites.

In this section, three examples are provided of the use data from two or more monitoring sites to provide evidence as to an emission source. These examples are:

1. Approximate location of H_2S sources using data from Dona Park CAMS 635, J.I. Hailey CAMS 630, Port Grain CAMS 629, and TCEQ Huisache CAMS 98.
2. The identification of ships as the source of elevated SO_2 at J.I. Hailey CAMS 630, Port Grain CAMS 629, and TCEQ Avery Point CAMS 6603 (which operated from August 2011 to December 2013).
3. The determination that certain alkane species were reaching the Corpus Christi area from outside the urban area, and most likely from oil and natural gas extraction activity some distance away.

Hydrogen Sulfide at Four Sites

Detectable concentrations of H_2S were measured over the course of the project at all H_2S monitors. The State of Texas maintains an 80 ppb 30-minute average concentration limit on any one emission facility. UT monitors were not regulatory instruments. Several sites did, however, measure H_2S exceedances of the State standard. Data were analyzed to attempt to isolate the key

upwind directions of potential emission sources. Figures 3-143 to 3-146 show the frequency over the course of the project that an H_2S measurement was greater than the 95th percentile H_2S value at the site within 10 degree wind direction bins, using coincident wind directions from the site. For example, in Figure 3-143, when the wind blew from around 210 – 230 degrees from 2005 through 2015, there was a strong chance – ≈70 percent – that an upper 5 percentile value would have been measured. So in Figures 3-147 and 3-148 on page 3-110, lines 20 degrees wide around the peak frequency directions from the line graphs have been drawn. In both figures, the directions converge to a cluster of equipment that may be an H_2S emission source.

Figure 3-143 Percent H_2S values > 95th percentile value at Port Grain CAMS 629 by wind direction

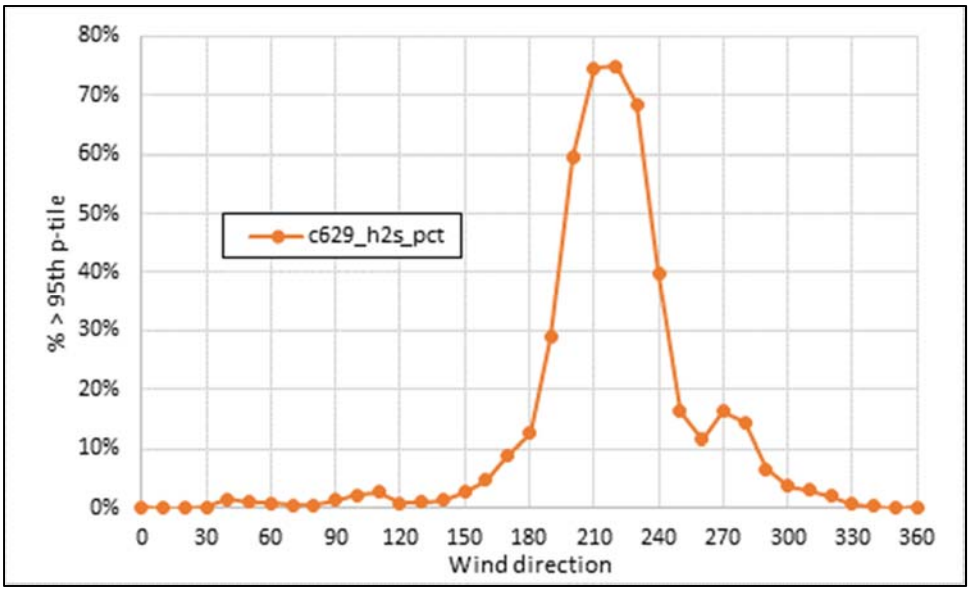


Figure 3-144 Percent H_2S values > 95th percentile value at J.I Hailey CAMS 630 by wind direction

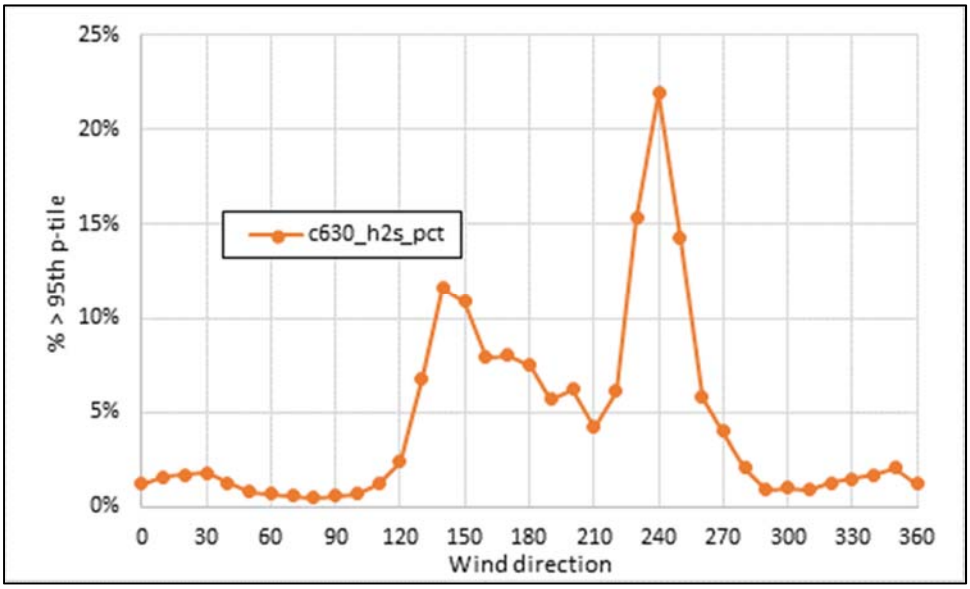


Figure 3-145 Percent H_2S values > 95th percentile value at Dona Park CAMS 635 by wind direction

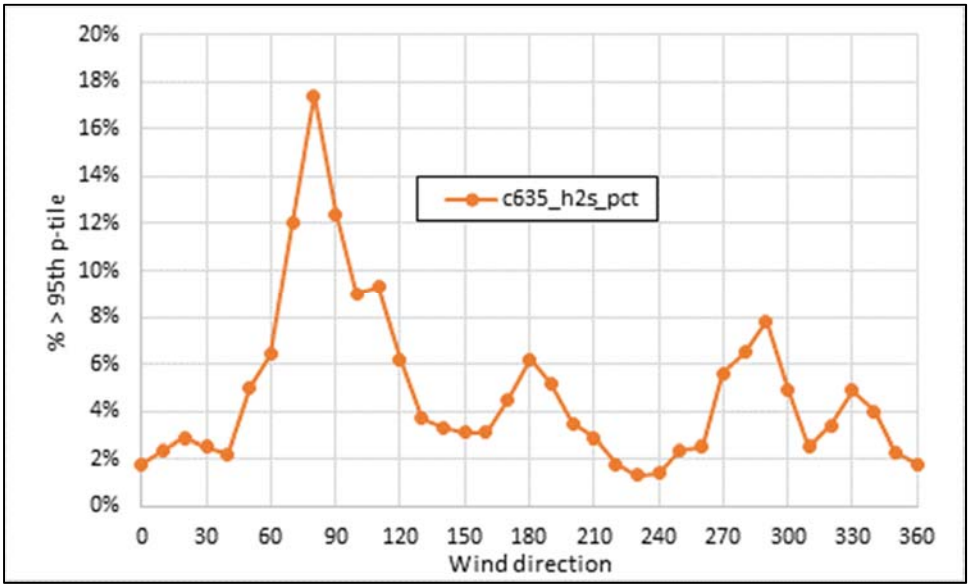


Figure 3-146 Percent H_2S values > 95th percentile value at TCEQ Huisache CAMS 98 by wind direction

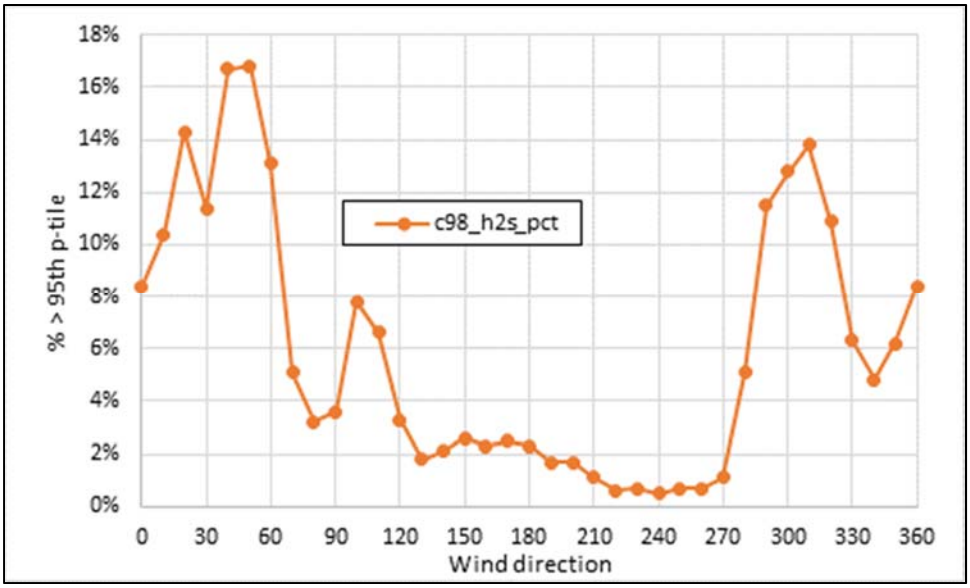


Figure 3-147 General upwind direction for elevated H_2S at three sites, rays based on peak directions from Figures 3-144, -145, -146

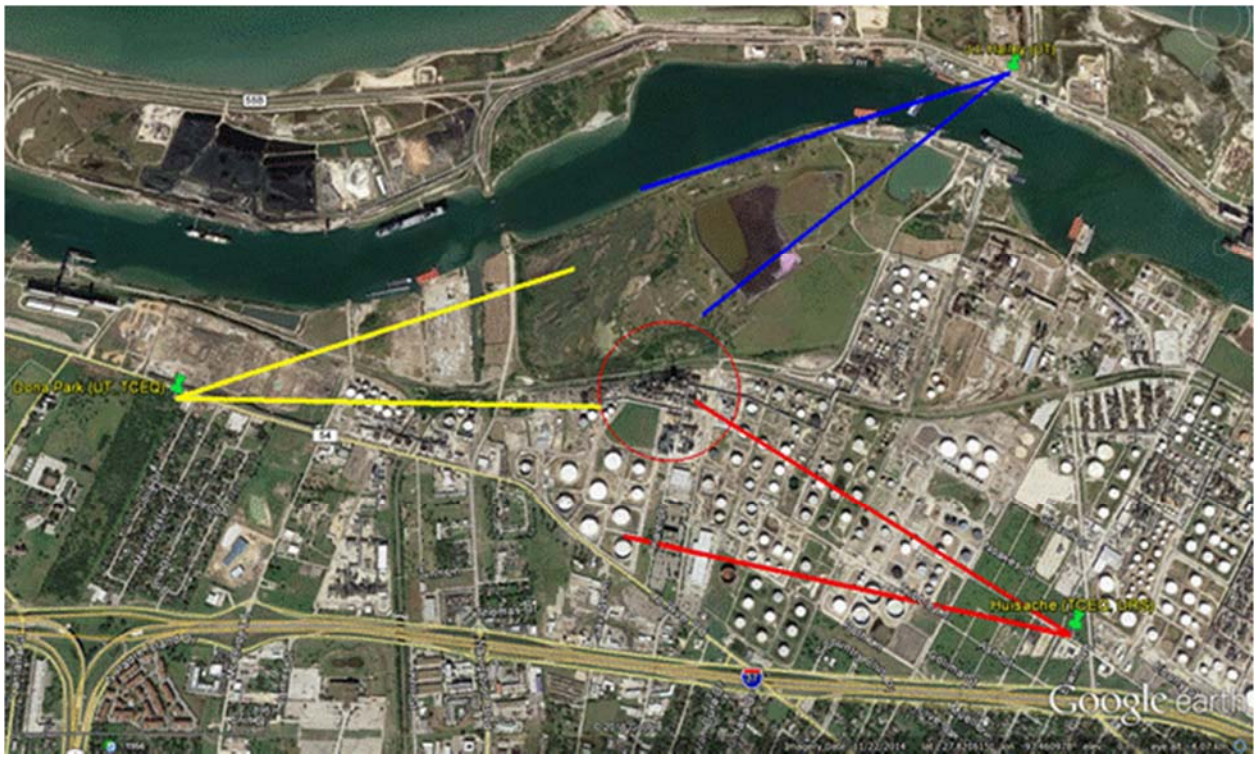
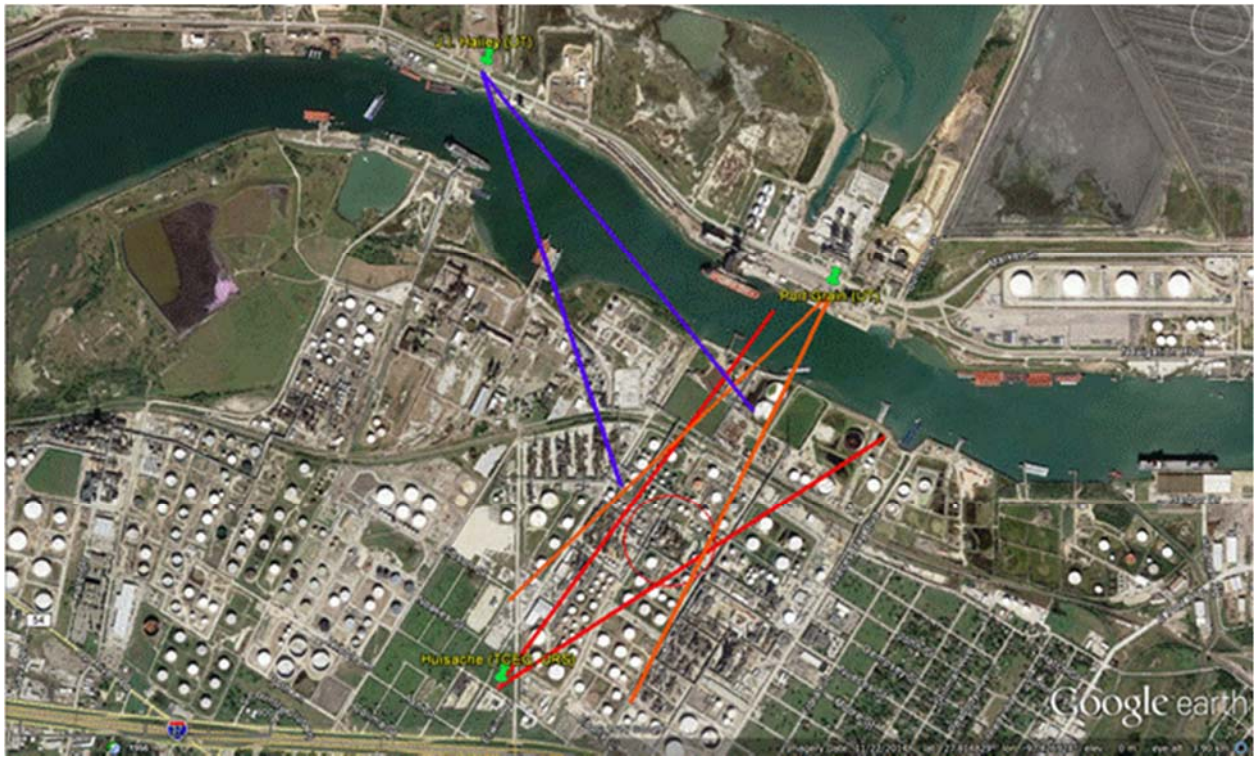


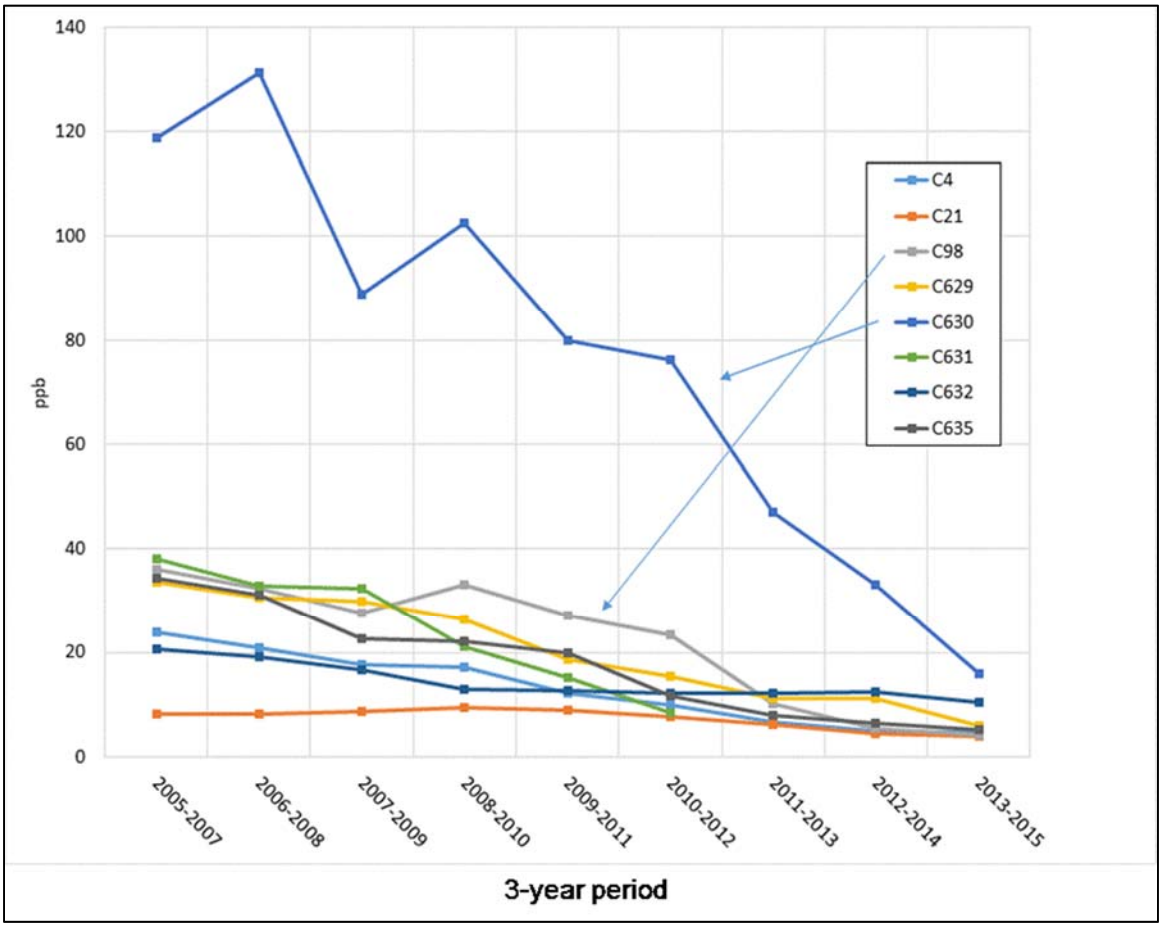
Figure 3-148 General upwind direction for elevated H_2S at three sites, rays based on peak directions from Figures 3-143, -144, -146



Sulfur Dioxide from Ships

As has been noted earlier, SO_2 concentrations at the J. I. Hailey CAMS 630 site were high enough, frequently enough, that the site did not comply with the U.S. EPA's National Ambient Air Quality Standard for SO_2. Over the course of the project, concentrations declined, as was the case with all monitoring sites in the area. This is reflected in Figure 3-149, showing all the NAAQS rolling three-year design values for each Corpus Christi monitoring site through the end of 2015, the last complete year of UT data.

Figure 3-149 Corpus Christi SO_2 Design Value Trends 2007 – 2015, J. I. Hailey CAMS 630 and TCEQ Huisache CAMS 98 are highlighted



The J. I Hailey and Port Grain sites both measured elevated SO_2 frequently when air blew from the south over the industrial area and ship docks. In August 2011, the TCEQ added a temporary monitoring site on the south side of the ship channel at Avery Point between the ship docks and the refineries. Figure 3-150 on page 3-112 shows the mean concentration of SO_2 by wind direction for the TCEQ Avery Point CAMS 6603 site for the second quarter of 2012 and for the second quarter of 2013. Figure 3-151 on page 3-112 shows the mean concentration of SO_2 by wind direction for the J. I. Hailey CAMS 630 site for the second quarter of 2012 and for the second quarter of 2013. It was in June 2012 that Federal new low-sulfur fuel rules for ships were put in place. There is a significant decrease in SO_2 concentrations by 2013 that has been

sustained through 2016. Directionality rays drawn from the two sites that intersect at the docks along the ship channel appear in Figure 3-152 on page 3-113.

Figure 3-150 Mean concentration of SO_2 by wind direction at Avery Point, second quarter 2012 and second quarter 2013.

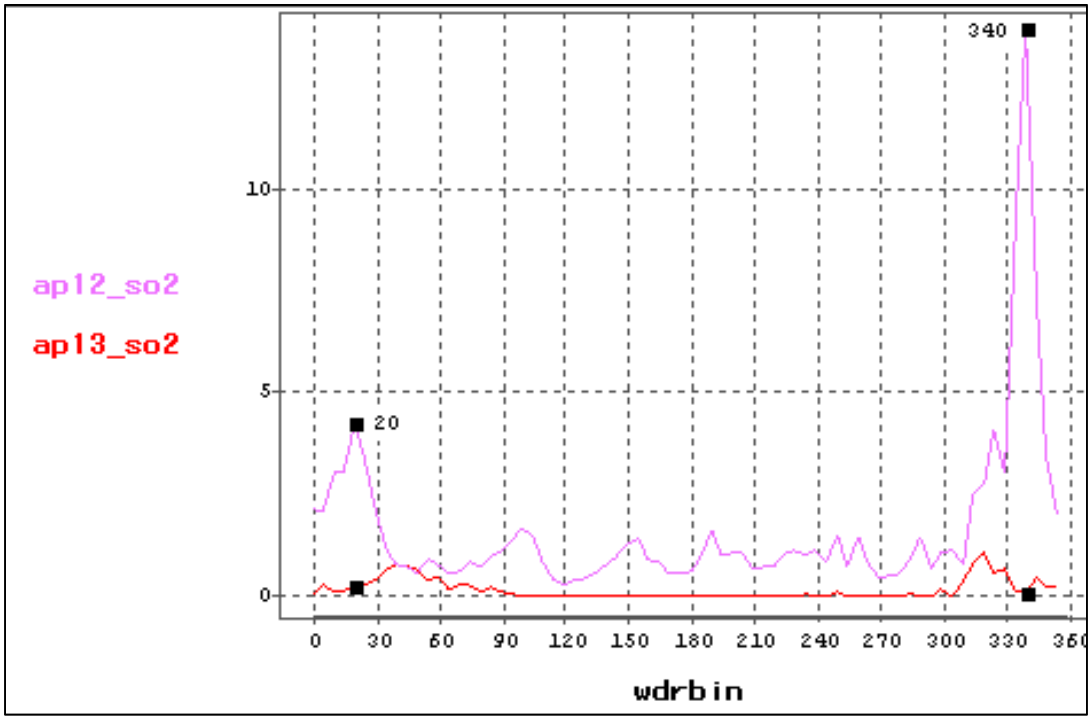


Figure 3-151 Mean concentration of SO_2 by wind direction at J. I. Hailey, second quarter 2012 and second quarter 2013.

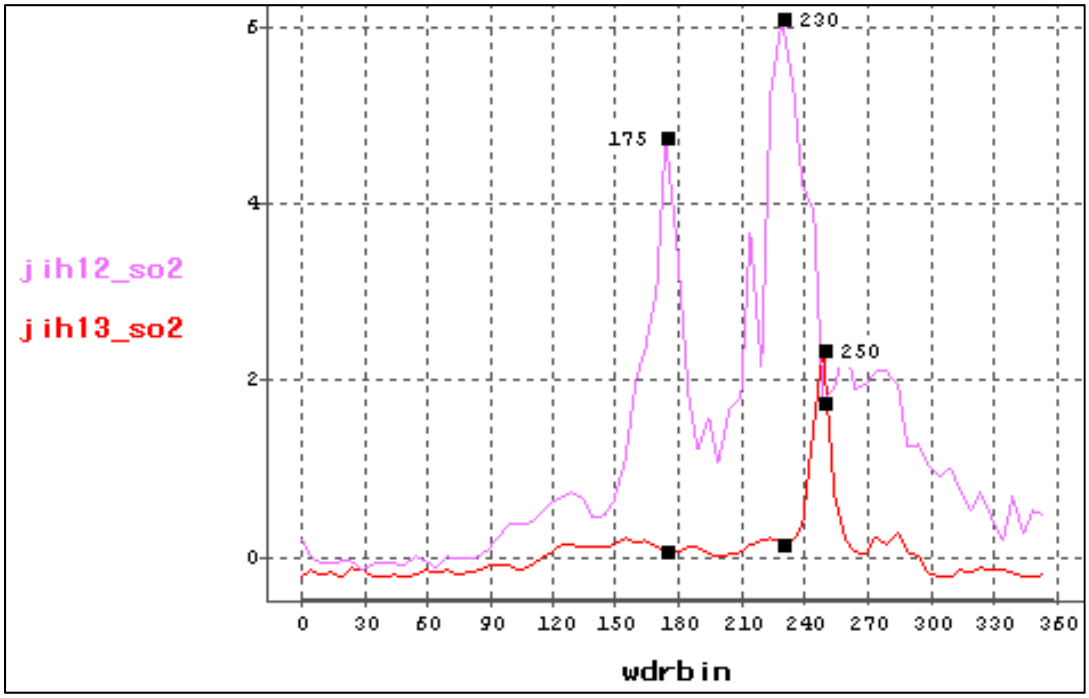
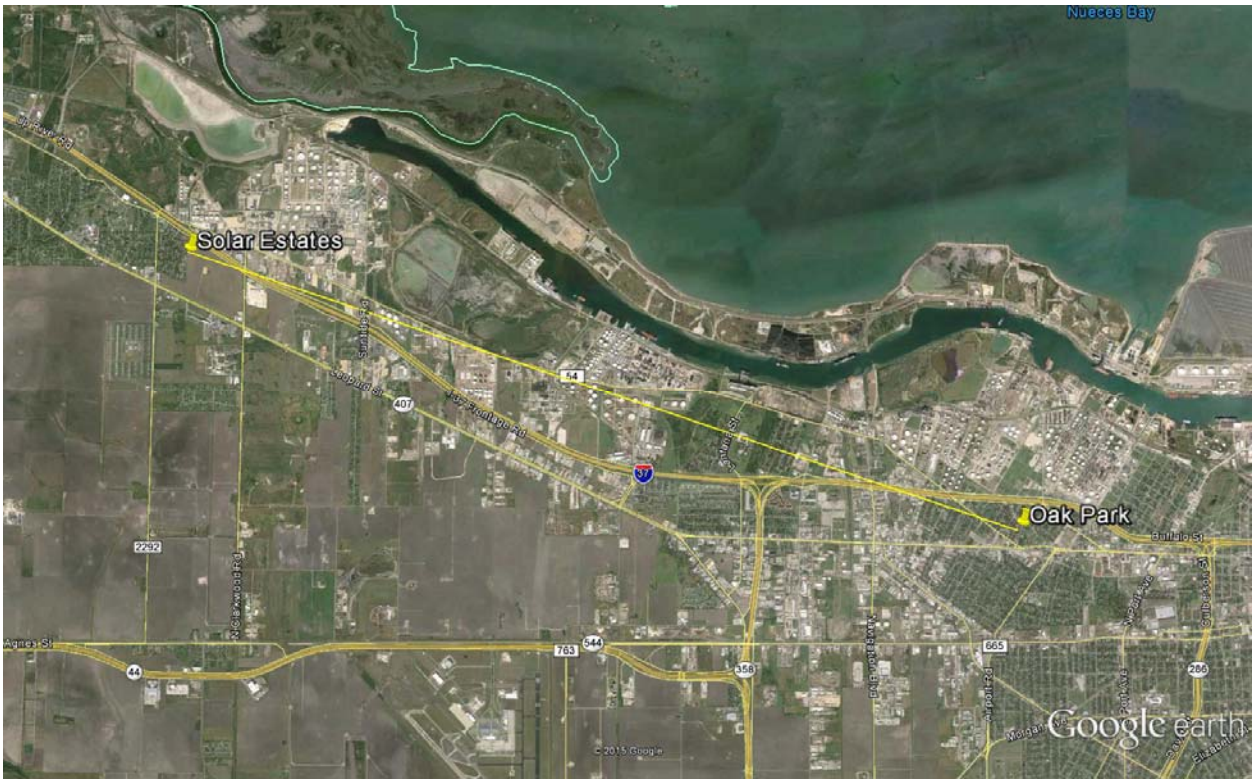


Figure 3-152 Peak mean concentration direction rays for JIH and Avery Point, white font for 2nd quarter 2012 and black font for 2nd quarter 2013. Possible that SO_2 peak in 2013 is ascribable to Dock 11.

Corpus Christi Ethane Concentration Characterization

Because of an upward trend in the concentrations of ethane, propane, and other light alkanes at the two project auto-GCs after 2012, as shown on earlier pages 3-68 and 3-88, several approaches were taken to investigate the trend. Both sites are shown in an aerial image in Figure 3-153 with a line segment of length 7.0 miles and heading of 108 degrees (east-southeast) from Solar Estates CAMS 633 to Oak Park CAMS 634.

Figure 3-153 Aerial image with Solar Estates and Oak Park auto-GC locations shown



The approach initially taken was to consider trends in the statistics describing the ethane data, which show approximately 30 to 40 percent increases in annual mean concentrations from 2009 to 2014. A second approach was to look at the surface winds and air parcel back-trajectories associated with higher than expected concentrations of ethane, which show northwesterly and northerly winds were key directions. Another approach was examining how often the two project auto-GCs measured elevated concentrations of ethane at the same time, compared to how often one site measured an elevated concentration and the other site did not. The rationale for this examination is as follows:

- If both sites measure an elevated concentration in the same hour, that may suggest that a distant source emitted ethane much earlier, and the concentrations spread out over a relatively large area.
- If one site measures an elevated concentration and in the same hour the other site measures a lower or typical concentration, that may suggest that a source near the first monitor emitted ethane earlier, and the concentrations did not sufficiently disperse to affect both monitors at the same time.

A preliminary finding is that the frequency of simultaneous measurements above the 95th percentile observation by hour has increased in recent years up to 2015, whereas the frequency of cases where one monitor measures a value above the 95th percentile while another has a measurement closer to its mean value has not changed noticeably.

For the first approach, UT used the data from 2009 and 2010 as the "baseline" period prior to the recent upward trend to establish monthly average "background" ethane concentrations for each site, sorted by wind direction, and UT used the 2013 and 2014 data as the more recent two years of complete data to assess how more recent data behaves relative to the baseline years. For labeling purposes, the 2013 and 2014 period is referred to as "recent". Only assessment from the Solar Estates site is considered in the next few figures for the sake of brevity. Figure 3-154 on page 3-116 shows the Solar Estates 2009-2010 baseline ethane mean concentrations in ppbC units by wind direction using April through September (spring and summer) data only, and Figure 3-155 on page 3-116 shows 2009-2010 baseline ethane mean concentrations by wind direction for January – March and October – December (winter and autumn) data only. Both figures use the same y-axis scale so the magnitudes of the mean concentrations can be compared across graphs. Owing in large part to meteorological factors, autumn and winter mean concentrations were generally higher at Corpus Christi sites than spring and summer mean concentrations.

Figures 3-156 and 3-157 on page 3-117 show graphs similar to those in Figures 3-154 and 3-155 using the "recent" 2013 – 2014 data. The spring-summer data in Figure 3-156 from the "recent" 2013-2014 period have mean concentrations roughly similar to those in Figure 3-154 from the "baseline" 2009-2010 period. However, there are noticeable differences between the autumn-winter "baseline" in Figure 3-155 and "recent" Figure 3-157 graphs, with higher mean concentrations in the latter.

Figure 3-154. Solar Estates 2009-2010 ethane mean ppbC "baseline" with spring / summer data

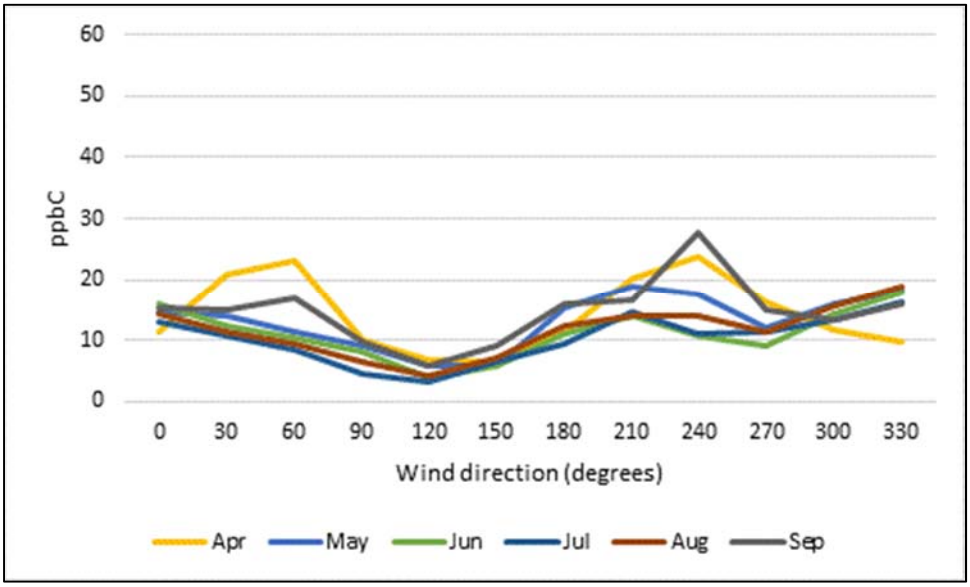


Figure 3-155. Solar Estates 2009-2010 ethane mean ppbC "baseline" with fall / winter data

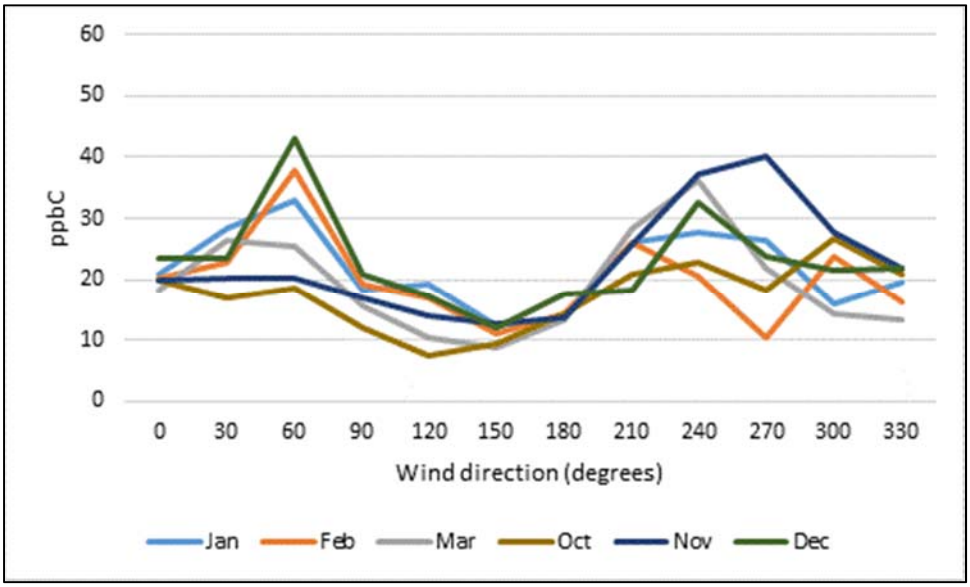


Figure 3-156. Solar Estates 2013-2014 ethane mean ppbC "recent" with spring / summer data

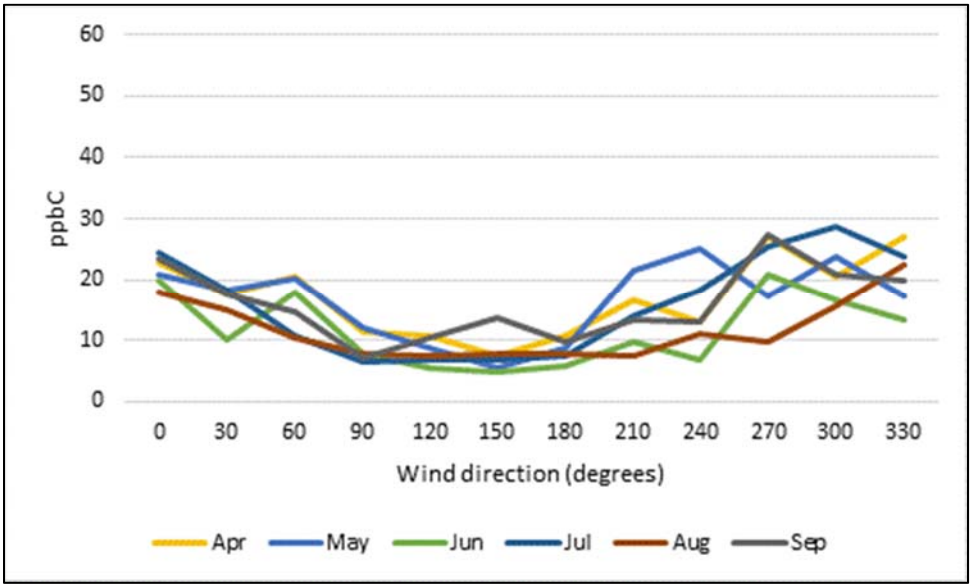
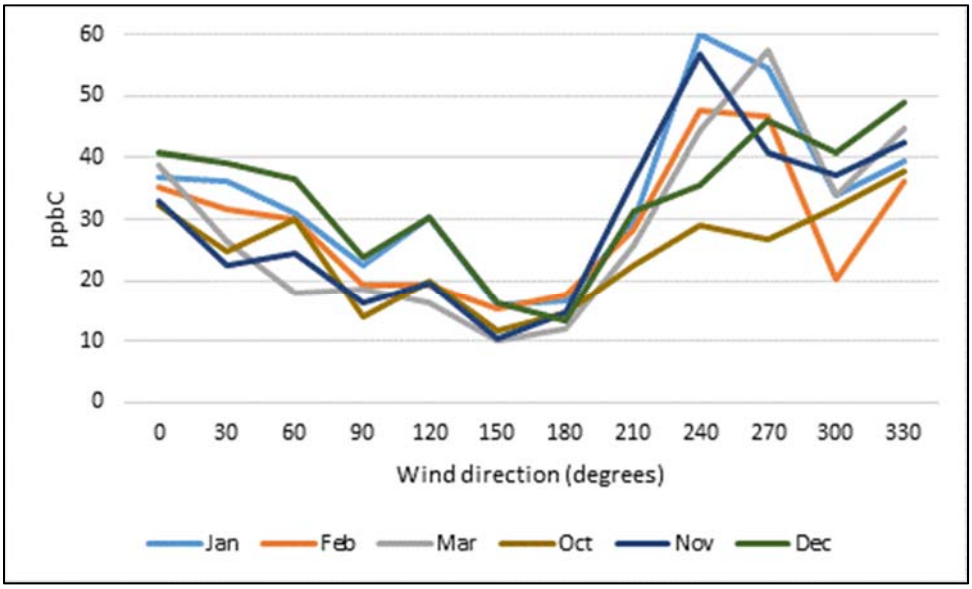


Figure 3-157. Solar Estates 2013-2014 ethane mean ppbC "recent" with fall / winter data



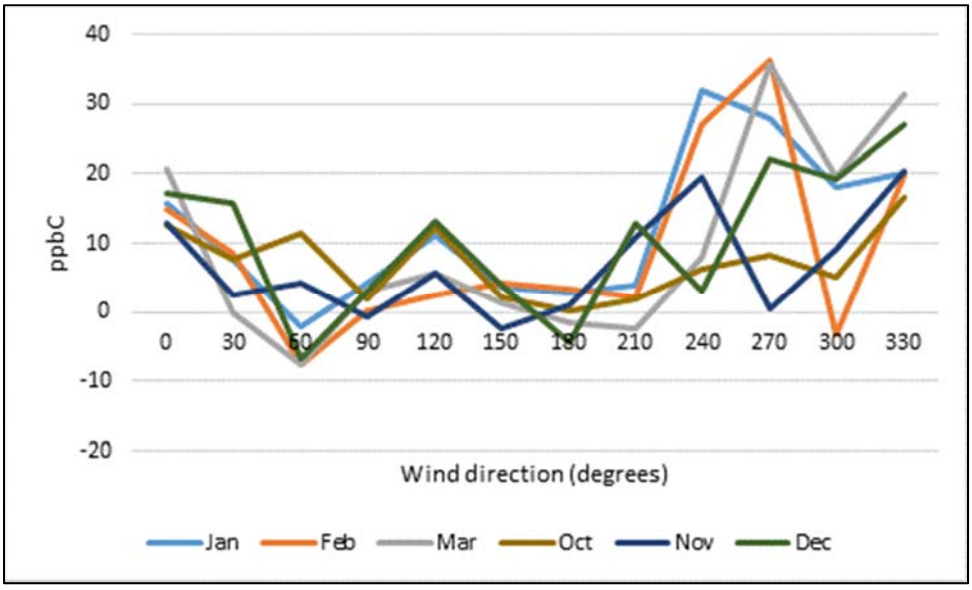
An assessment for how much change has occurred in ethane mean concentrations at Solar Estates on an annual basis between 2009 and 2014 is shown in Table 3-5 on page 3-118. This table shows the slopes of lines fit to time-period comparisons for the change from 2009-2010 to 2011-2012 and from 2011-2012 to 2013-2014, expressed as ppbC / year, by 30-degree wind direction bin and by month of the year. The table has cells color-coded by the intensity in the change. The largest changes are to the west (240 and 270 degrees) in December through March and north-northwest (330 degrees and 0 degrees) in October through April.

The "enhancement" or difference (the 2013-2014 value minus the 2009-2010 value) in the graphs in Figures 3-155 and 3-157 on pages 3-116 and 3-117 is shown by month and by wind direction in Figure 3-158 below. On would note that the largest enhancement is from the west through north, which is the general direction to the Eagle Ford Shale region that saw an increase in gas and oil activity in 2012 and later.

Table 3-5. Solar Estates slopes of three time-period comparisons, average change 2009-2010 to 2011-2012 and 2013-2014, expressed as ppbC / year, by 30-degree wind direction bin and month of year, color coded (redder for more positive, greener for more negative)

Wind dir. bin	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
0	3.98	3.74	5.18	2.88	1.60	0.91	2.90	0.85	2.06	3.12	3.26	4.29
30	1.92	2.16	-0.01	-0.85	1.03	-0.56	1.85	0.90	0.68	1.96	0.60	3.94
60	-0.51	-1.88	-1.88	-0.62	2.22	1.93	0.62	0.23	-0.60	2.87	1.09	-1.69
90	1.07	0.04	0.80	0.37	0.67	-0.09	0.50	0.35	-0.60	0.49	-0.16	0.79
120	2.78	0.61	1.45	1.00	0.73	0.47	0.90	0.79	1.12	3.10	1.40	3.30
150	0.91	1.09	0.36	0.27	-0.05	-0.19	0.07	0.19	1.10	0.55	-0.62	1.02
180	0.71	0.82	-0.36	-0.18	-1.66	-1.36	-0.46	-1.14	-1.54	0.09	0.29	-1.07
210	0.97	0.57	-0.63	-0.86	0.68	-1.06	-0.16	-1.63	-0.86	0.48	2.72	3.26
240	8.01	6.76	2.04	-2.69	1.88	-0.95	1.76	-0.71	-3.68	1.55	4.88	0.78
270	6.99	9.07	8.93	2.68	1.32	2.91	3.54	-0.44	3.13	2.07	0.15	5.56
300	4.49	-0.83	4.90	2.16	1.98	0.61	3.77	-0.06	1.86	1.30	2.31	4.85
330	5.03	4.96	7.82	4.33	-0.25	-1.13	1.90	0.90	0.95	4.20	5.14	6.79

Figure 3-158. Solar Estates 2013-2014 ethane "Enhancement" over 2009-2010 for fall & winter



A question to ask is: In what manner has the mean concentration for ethane changed? According to Figure 3-158, at Solar Estates the concentration under winds from the west through north in fall and winter months led to a large part of the increase. The increase could have come from, say, a constant increase in every measurement from the west of 30 ppbC, or could have been due to a relatively small number of very high concentrations that had influenced the mean to increase. Figures 3-159 and 3-160, on page 3-120, show the mean concentrations of ethane by hour for the baseline 2009-2010 and recent 2013-2014 periods for Solar Estates and Oak Park, respectively. One method to examine this is to look at the statistical distributions of the data. For example, if all else is held equal, and every measurement was higher by 4 ppbC, then the mean and median values would rise by 4 ppbC. If, however, a relatively few very high values caused the mean to rise by 4 ppbC, the median, which is the point in rank ordering of the data for which half the values are larger and half are smaller, would change very little if at all. Figures 3-161 and 3-162, on page 3-121, show the median concentrations of ethane by hour for the baseline 2009-2010 and recent 2013-2014 periods for Solar Estates and Oak Park, respectively. These graphs show changes on the order of 1 ppbC increase by hour during the daytime hours, with larger differences in the early morning hours. Figures 3-163 and 3-164, on page 3-122, show the cumulative distributions for the ethane data at 15 CST (3 pm CST) for Solar Estates and Oak Park, respectively, for the two periods. The fact that the baseline and recent graphs are similar up to the 50 percent point (the median) and then diverge from there suggests that it is an increase in the upper percentile measurements that is strongly affecting the averages at the sites.

Figure 3-159. Solar Estates mean ethane concentrations 2009-2010 (blue) and 2013-2014 (orange)

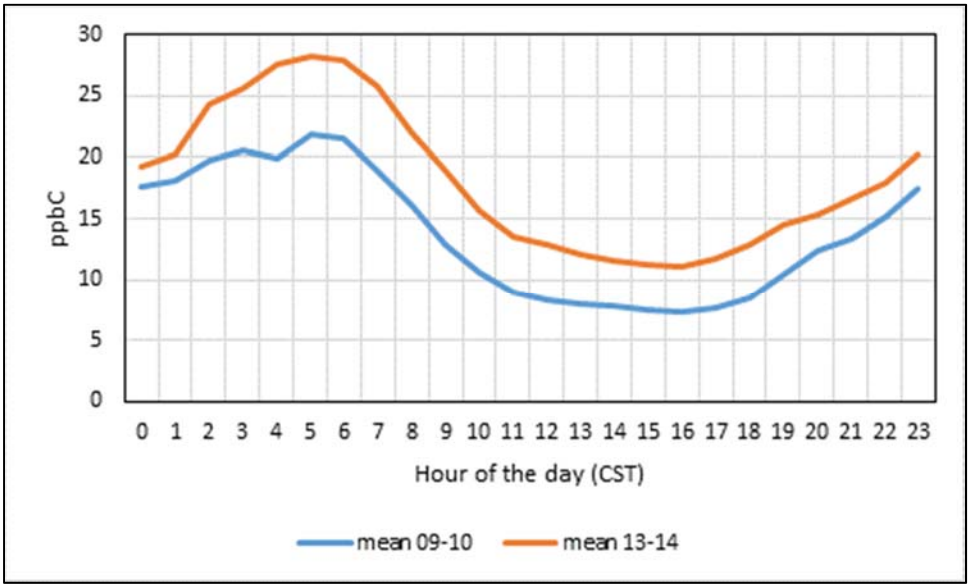


Figure 3-160. Oak Park mean ethane concentrations 2009-2010 (blue) and 2013-2014 (orange)

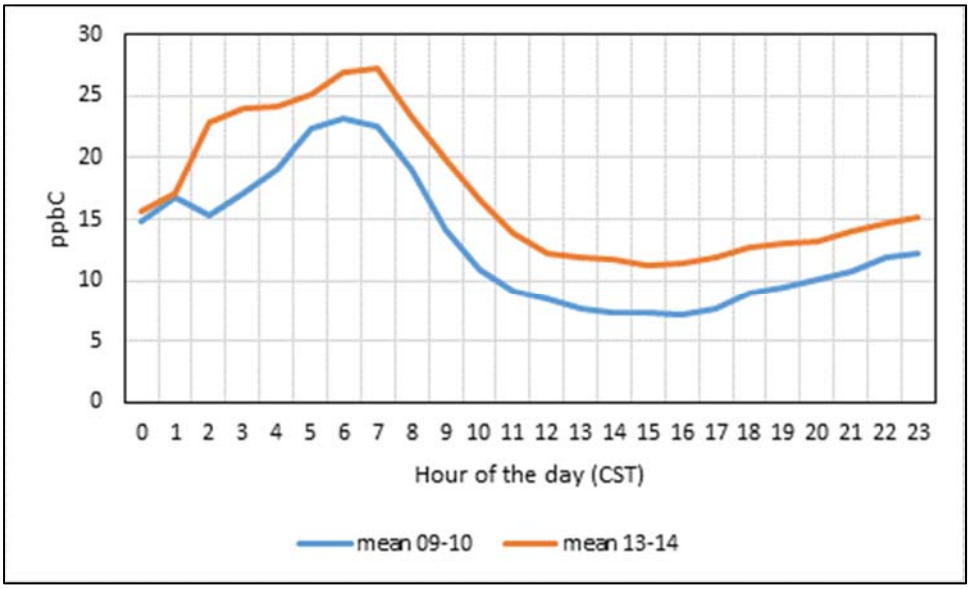


Figure 3-161. Solar Estates median ethane concentrations 2009-2010 (blue) and 2013-2014 (orange)

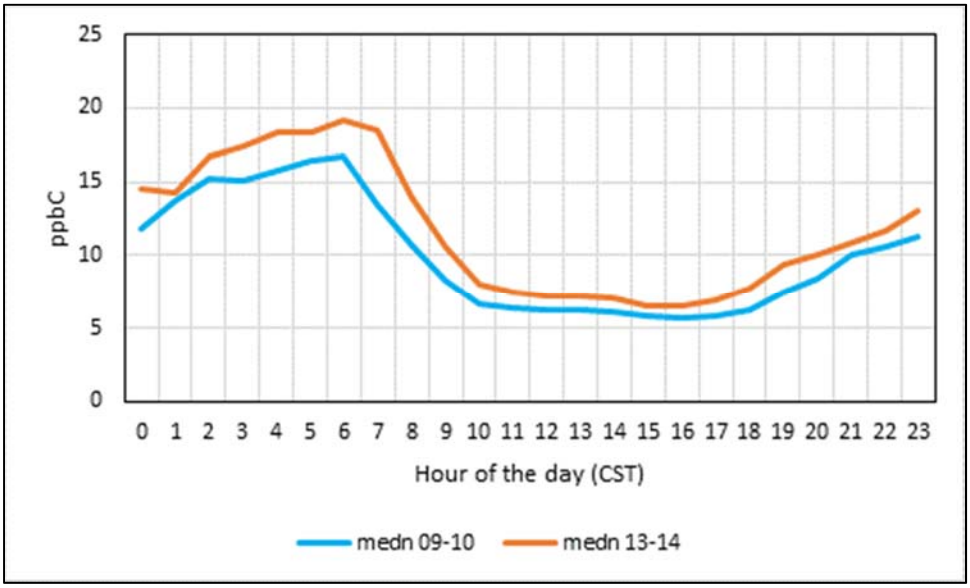


Figure 3-162. Oak Park median ethane concentrations 2009-2010 (blue) and 2013-2014 (orange)

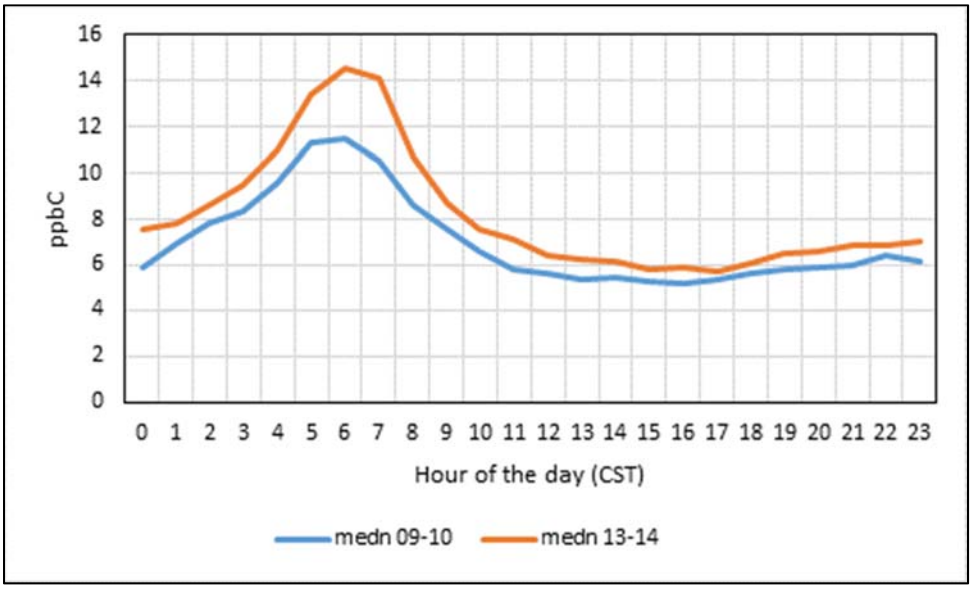


Figure 3-163. Solar Estates cumulative distribution at 15 CST (3 pm CST) 2009-2010 (blue) and 2013-2014 (orange)

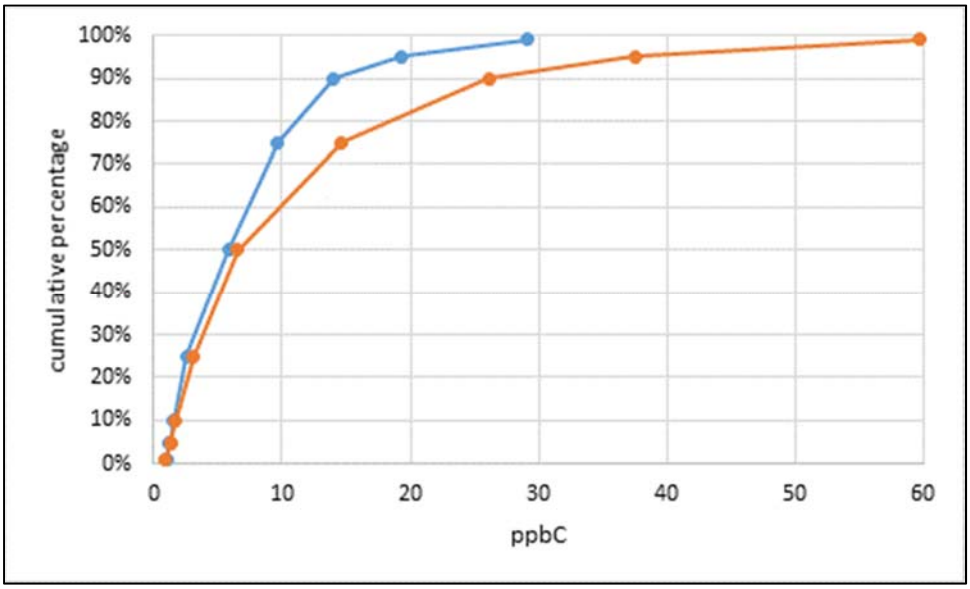
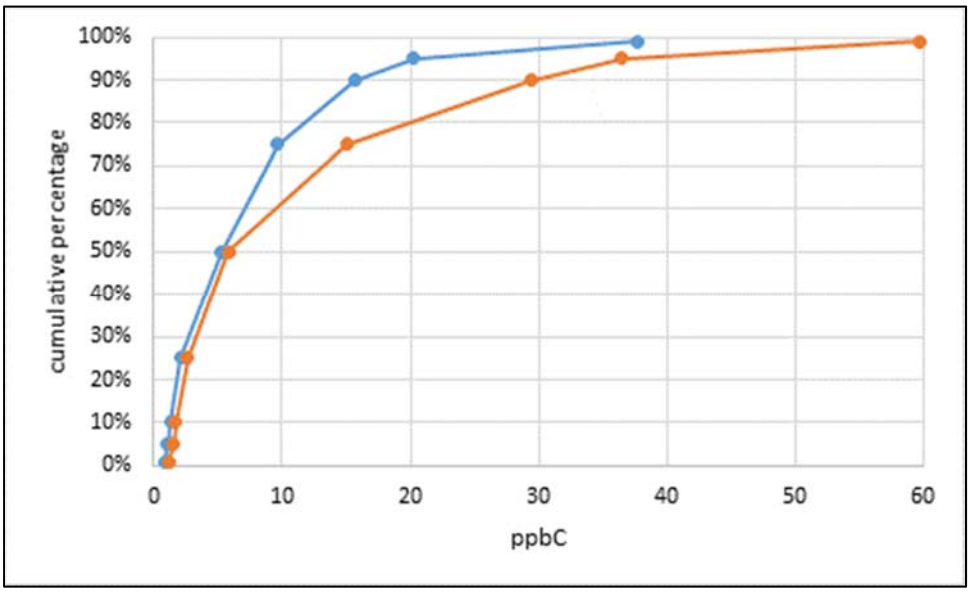


Figure 3-164. Oak Park cumulative distribution at 15 CST (3 pm CST) 2009-2010 (blue) and 2013-2014 (orange)



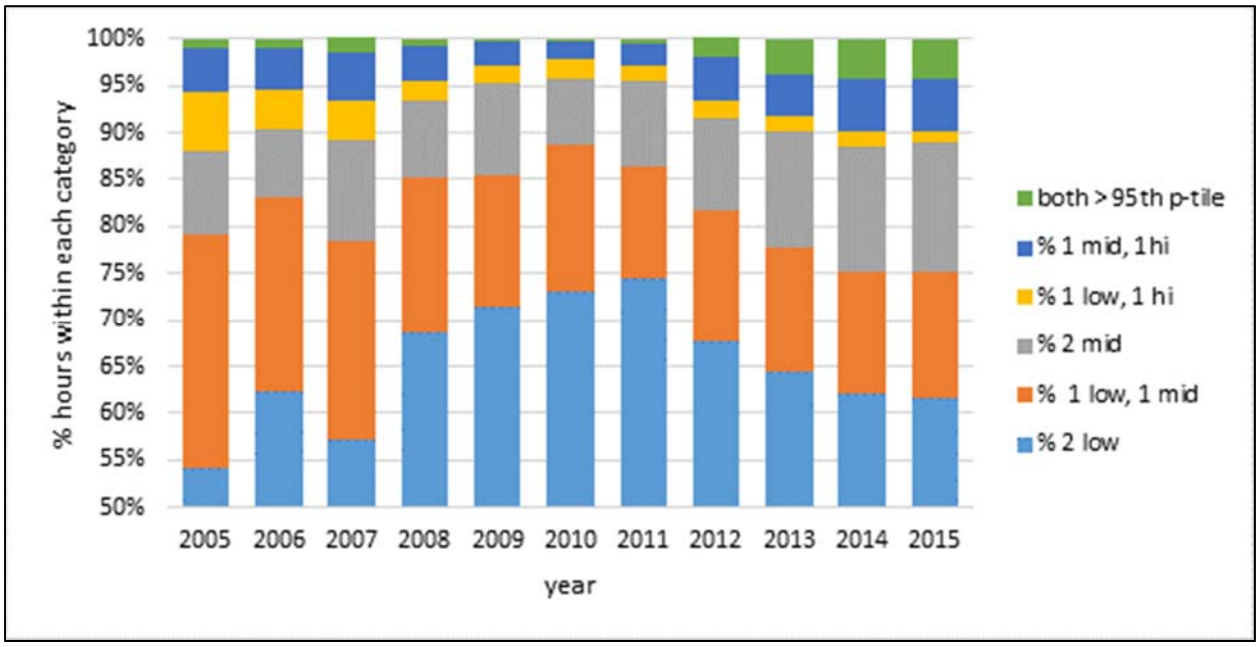
To study the trends in the upper percentiles in the data, the 95th and 75th percentiles in the ethane data from Solar Estates and Oak Park were calculated for each quarter of the year (to account for seasonality) and every hour of the day (to account for the diurnal pattern) over the years from 2005 through 2015.

Next, using data from both Solar Estates and Oak Park, the frequency during 2005 through 2015 period when the following events occurred were tabulated:

a. For each time step, neither site simultaneously observed a concentration higher than the **75th** percentile concentration for that hour and annual quarter for that site: "2 low".
b. For each time step, one of the two sites observed a concentration higher than the **75th** percentile concentration but less than the **95th** percentile concentration for that hour, while the other measured a concentration less than the **75th** percentile concentration for that hour and annual quarter: "1 low, 1 mid"
c. For each time step, both of the two sites observed a concentration higher than the **75th** percentile concentration but less than the **95th** percentile concentration for that hour and annual quarter: "2 mid"
d. For each time step, one of the two sites observed a concentration higher than the **95th** percentile concentration for that hour, while the other measured a concentration less than the **75th** percentile concentration for that hour and annual quarter: "1 low, 1 hi"
e. For each time step, one of the two sites observed a concentration higher than the **95th** percentile concentration for that hour, while the other measured a concentration greater than the **75th** percentile concentration but less than the **95th** percentile concentration for that hour and annual quarter: "1 mid, 1 hi"
f. For each time step, both sites observed a concentration higher than the **95th** percentile concentration for that hour and annual quarter: "both > 95th p-tile"

The conclusion from such a classification of hours may be that event (f) for simultaneous elevated concentrations would represent a likely transport for ethane from some distance allowing dispersion enough to simultaneously affect two sites miles apart. Conversely, event (d) in which one site is affected to a practically more significant extent than the other, suggests a more local emission source was prominent. Figure 3-165 on page 3-124 shows a bar graph that shows the percentage of hours in each of the six categories listed above.

Figure 3-165 Bar chart of the distribution of categories for each hour of coincident ethane data for two UT auto-GCs by year relative each site's 75th and 95th percentile by hour and annual quarter 2005 – 2015



The findings from this are that the biggest change appears to be when both sites simultaneously measure elevated values; i.e., both sites in the top 5 percent of measurements by hour and quarter. Again, as stated earlier, if two sites 7 miles apart have elevated concentrations at the same time, it is likely that the emission source was relatively far away.

One way to gauge the scale of the enhancement to ethane concentrations is to consider the integration of the time series for ethane, by summing up concentrations within a time period to produce a total in units of ppbC-hours. Consider the two time series graphs in Figures 3-166 and 3-167, page 3-125, for ethane data at Solar Estates and Oak Park over a two-week summer period in 2010 and the same two-week period in 2014. In the second graph, it is clear that there is a large background concentration of ethane that persisted in the Corpus Christi area from August 2 to August 6, 2014 affecting both sites. Integrating under the time series in Figure 3-166 for Solar Estates produces 3,030 ppbC-hrs, using linear interpolation to fill in values missing for daily quality assurance samples. Similarly, data in Figure 3-167 produce 3,219 ppbC-hrs for Solar Estates, which is a 6.2 percent enhancement. This may or may not be a representative pair of two week periods; however, it was not difficult to find cases with sustained ethane concentrations significantly higher than the long run average concentration for a given hour/quarter after 2012.

Figure 3-166 Sample two-week time series for ethane from 2010 at Solar Estates and Oak Park

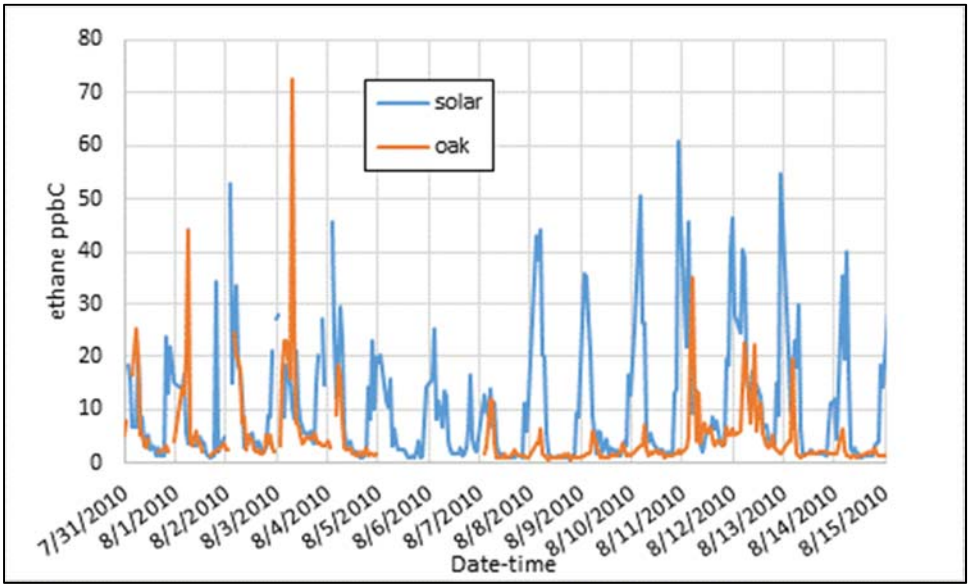
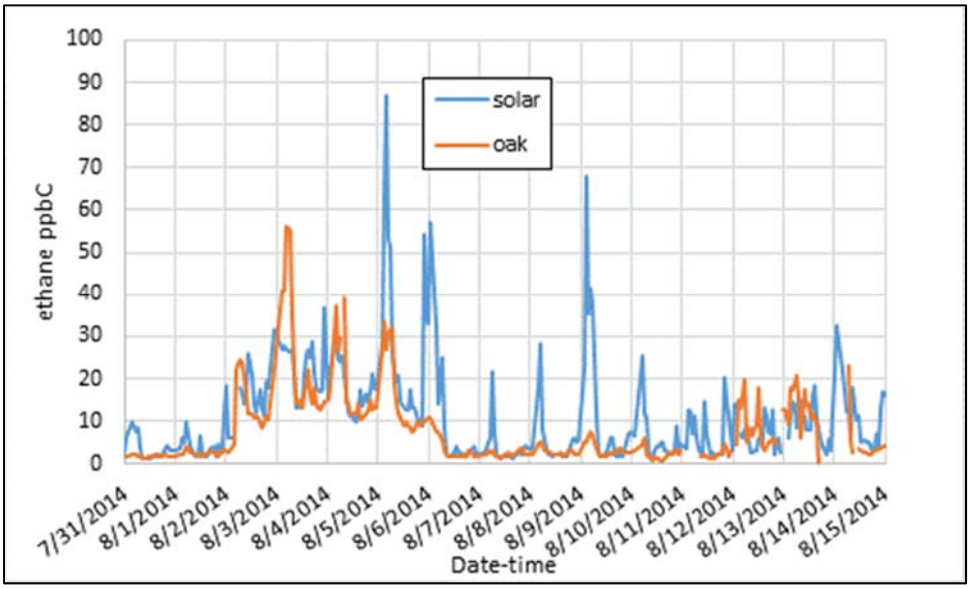


Figure 3-167 Sample two-week time series for ethane from 2014 at Solar Estates and Oak Park



3.6 Results of Canister Sampling

Canister sampling was initially conducted at all seven original CAMS sites when TNMHC concentrations exceeded 2,000 ppbC for 900 consecutive seconds (15 minutes). In February 2009, UT Austin ended the practice of triggering canister samples at the auto-GC sites, because those sites already took hourly hydrocarbon samples, and the marginal benefits of also taking canister samples was felt to be of insufficient value. Also, at the outset of the project, up to three canister samples of different sample durations would be triggered by elevated hydrocarbon measurements and this practice ended in 2007 and was replaced with a protocol in which one 20-minute duration canister sample would be triggered. For comparability, the data described herein is from 2007 and later from the five CAMS sites that continued canister samples up until

decommissioning. In 2012 – 2016, canisters could be triggered at the J. I. Hailey by SO_2 concentrations greater than 50 ppb.

3.6.1 Graphs of canister samples

Bar charts and electronic spreadsheets of all canister samples are available on request. Some examples have been provided earlier in this report for the J. I. Hailey CAMS 630 site.

3.6.2 Benzene in canister samples

A summary of the number of canister samples and maximum benzene concentrations in canister samples by site appears in Table 3-6, below. The top 10 canister samples for benzene since 2007 from the five sites are listed in Table 3-7, below.

Table 3-6. Summary of canister sample counts and maximum benzene concentrations 2007 - 2016

Row Labels	Count of canisters	Max of benzene
CCG CAMS 629	64	196.0
DPK CAMS 635	109	60.6
FHR CAMS 632	24	31.2
JIH CAMS 630	140	407.3
WEH CAMS 631	25	17.3
Grand Total	**362**	

Table 3-7. Top 10 benzene concntrations from canister samples

Site name	date	Time start CST	Benzene ppbV
JIH C630	1/27/2007	18:41	392.83
JIH C630	3/6/2007	4:02	407.25
JIH C630	10/18/2007	1:13	35.69
JIH C630	9/27/2008	4:57	31.44
FHR C632	1/13/2008	0:36	31.19
DPK C635	12/14/2009	22:46	60.55
CCG C629	5/10/2007	4:48	196.01
CCG C629	7/7/2007	23:34	28.86
CCG C629	2/16/2010	23:45	41.72
CCG C629	10/23/2012	7:43	118.29

In 2007, J. I. Hailey and the Port Grain sites measured benzene concentrations greater than the TCEQ's short-term AMCV. The TCEQ's Toxicology Division annually reports on the results of air quality monitoring in Texas. In their evaluation of the 2007 data in Texas they reported the following (https://www.tceq.texas.gov/assets/public/implementation/tox/monitoring/evaluation/2007/reg_14_corpus.pdf accessed August 2016):

“Reported short-term benzene levels measured at the J. I. Hailey and the Port Grain Elevator monitoring sites through the CCAQP exceeded the TCEQ’s short-term health-based comparison value of 180 ppbV. The weight of scientific evidence indicates that short-term exposures to the measured benzene levels would not be expected to cause adverse health effects. However, frequent short-term exposures to the highest reported concentrations or exposure to higher concentrations would reduce the margin of safety afforded by the comparison values.”

3.6.3 Comparing canister samples to continuous TNMHC measurements

One method of quality assurance is to compare the measurements made simultaneously by two different instruments or by two different analysis methods. Using 326 canister samples triggered on elevated TNMHC, Figure 3-168, below, shows the results of comparing the sum of all identified individually measured hydrocarbon species concentrations for each canister with the simultaneously measured total nonmethane hydrocarbon concentration from the TNMHC analyzer quantified in real time. A small number of outliers existed with significant disagreement between the canister and coincident TNMHC. Figure 3-169, page 3-129, shows the results of comparing the sum of canister species with coincident TNMHC with 10 samples (3% of samples) not used. The R^2 value, which represents the fraction of the variance in the canister data explained by the regression on the TNMHC analyzer, changes from 0.80 to 0.94 between Figure 3-168 and 3-169. The same change in data reduces slope from 0.93 to 0.83. It is expected that the sum of known species would be less than the TNMHC, as suggested by the slope being less than 1.00, as the canister sum does not include unidentified species. Overall this agreement is very good and provides confidence in both canister measurements and TNMHC measurements.

Figure 3-168. Comparison between the total mass of known canister hydrocarbons with simultaneously collected continuous TNMHC measurements, 326 canister samples, 2007 - 2016

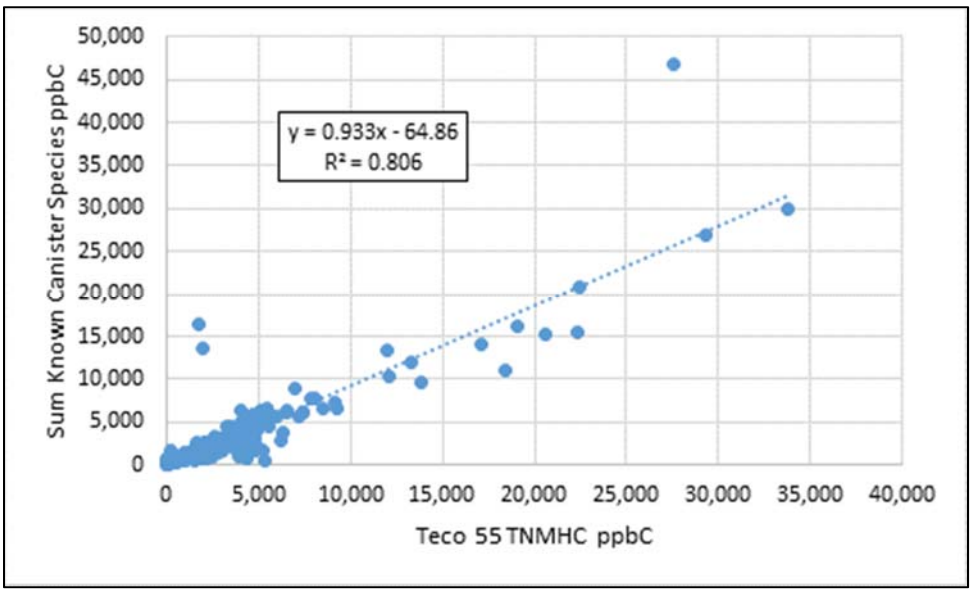
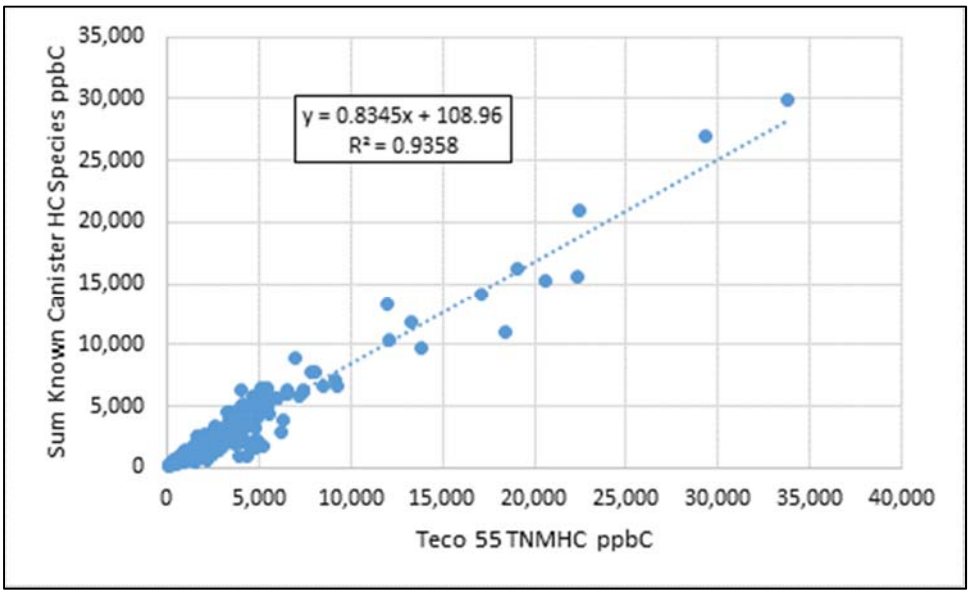


Figure 3-169. Comparison between the total mass of known canister hydrocarbons with simultaneously collected continuous TNMHC measurements, 316 canister samples, 2007 - 2016



To illustrate how this comparison between the canisters and TNMHC analyzers is done, Table 3-8, page 3-130, shows several of the five-minute time scale measurements taken at the J. I. Hailey CAMS 630 site on June 2, 2015, a day on which a canister sample was taken. The first row in Table 3-8 shows that in the five-minute period from 12:55:00 a.m. CST to 12:59:59 a.m. CST (shown as 0:55 CST), the flow of air to the canister (volumetric flow) was close to 0.0 milliliters/minute (ml/min) and the pressure in the canister was close to 0 pound per square inch atmospheric (psia), or a near-vacuum. When a canister is filling, the instantaneous flow rate is approximately 15 ml/min. Since each record is a five-minute average, if a canister starts to fill with air, say, half-way into a 5-minute period, then the reported flow for that five-minute period would be around 7.5 ml/min. The second row in Table 3-8 shows that during the five-minute period from 1:00:00 a.m. CST to 1:04:59 a.m. CST, the volumetric flow averaged 11.2 ml/min and the pressure in the canister had risen to an average 1.2 psia. This implies that in this five-minute period, a canister sample was triggered and air had started to flow into the canister. As was mentioned above, the instantaneous flow rate is approximately 15 ml/min, so if an average over a set five-minute period is only 11.2 ml/min, and the rate was 15 ml/min, then the flow happened over 3 minutes and 44 seconds (5 min. × 11.2/15 = 3.67 = 3 min. 44 sec.). This implies the canister started filling close to 1:01:16a.m. CST (1 minute 16 seconds plus 3 minutes 44 seconds equals 5 minutes). According to the field data sheet for this canister sample, the canister was triggered at 1:01 a.m. CST, confirming this calculation.

The next three rows in Table 3-8 show that during the five minute periods starting at 1:05 a.m. CST, 1:10 a.m. CST, and 1:15 a.m. CST, the volumetric flow averaged 14.8 (which is approximately 15) ml/min and the pressure in the canister rose ~3 psia/5-minute period. The next row in Table 3-8 shows that five-minute periods starting at 1:20 a.m. CST the average volumetric flow dropped to 6.7 ml/min, implying that air flowed to the canister for approximately 2 min. 14 seconds (5 min. × 6.7/15 = 2.23). Thus, overall the air flowed into the canister from 1:01 CST to 1:22 CST, approximately 20 minutes. The last two rows with sample

start times 1:25 and 1:30 CST show mass flow has returned to 0.0 ml/min and the canister pressure is approximately unchanged at just below the standard atmospheric pressure of 14.5 psia, showing no air is flowing to the canister.

The method for estimating the average TNMHC concentration during the canister sample is to add the products of the volumetric flow ml/min and the TNMHC values, for the periods with positive flow, and then divide the result by the sum of the positive flows. This provides an average TNMHC value weighted by the volumetric flow. The actual sum of hydrocarbon species in the canister sample on June 2 corresponding to this example was 3,508 ppbC. The weighted volumetric flow derived from Table 3-8 is given by

$$(11.2\times4{,}958+14.8\times4{,}110+14.8\times4{,}140+14.8\times2{,}776+6.7\times1{,}314)/(11.2+14.8+14.8+14.8+6.7) = 3{,}652 \text{ ppbC}$$

The difference in this comparison, which was chosen at random from the 316 canisters, is only 4 percent.

Table 3-8. J. I. Hailey CAMS 630 five-minute time scale values, early on June 2, 2015

Time CST	Volumetric flow ml/min	Can Pressure psia	SO_2 ppb	H_2S ppb	TNMHC ppbC	Methane ppb	Wind speed mph	Wind direction deg.
0:55	0.0	0.2	-1.3	0.9	5,914	2,433	7.8	213.2
1:00	**11.2**	1.2	-1.3	1.9	4,958	2,309	7.5	208.3
1:05	**14.8**	4.3	-1.5	2.7	4,110	2,180	7.5	207.9
1:10	**14.8**	7.5	-1.7	1.9	4,140	2,364	6.9	214.3
1:15	**14.8**	10.7	-1.7	1.7	2,776	2,389	7.9	210.8
1:20	**6.7**	13.3	-1.4	1.4	1,314	2,265	7.1	212.3
1:25	0.0	13.6	-1.7	1.2	778	2,548	7.3	213.3
1:30	0.0	13.6	-1.6	1.2	882	2,294	7.3	213.3

3.7 Conclusions

From December 2004 through May 21, 2016, The University of Texas at Austin Center for Energy and Environmental Resources operated a network of air quality and meteorological monitoring stations in the Corpus Christi, Texas industrial area. During the past two years, UT Austin made several efforts to acquire additional resources to extend the monitoring, and had success in receiving funding from the TCEQ for at least one year of continued operation of two sites, with reductions in the instrumentation at those two sites.

The overall findings of this study are as follows:

- The pollution sources that affect Corpus Christi monitors were often local emission sources, including sources located within a few hundred feet from some sites. Other times the sources were the large industrial sources and ships within Nueces County. Finally there is evidence that emissions sources outside the region, including emissions from the Eagle Ford oil and gas production region, may have added to measured concentrations, particularly after 2012.

- Benzene concentrations at the two project monitoring sites, in residential areas, which made hourly measurements of individual hydrocarbons (Solar Estates and Oak Park), declined after the first three years of the project and had relatively little variation over the subsequent eight years. The highest concentrations were observed at times when the sites were downwind of the refinery area.

- Concentrations of hydrocarbons at the residential monitoring sites that made hourly measurements of hydrocarbons have on rare occasions exceeded odor threshold air monitoring comparison values (AMCV) established by the Texas Commission on Environmental Quality (TCEQ), but have not exceeded any long-term health AMCV. Concentrations of hydrocarbons have on rare occasions exceeded TCEQ short-term AMCV, but not since 2007.

- There has been a general downward trend in mean concentrations for most hydrocarbon species at the residential monitoring sites that made hourly measurements of hydrocarbons (Oak Park and Solar Estates); however, the downward trend for several low-molecular weight low-reactivity alkane species was reversed around 2012, followed by decline in 2015. These changes are hypothesized to be related to changes in natural gas extraction activities, largely in regions north of Corpus Christi.

- At one of the residential monitoring sites that made hourly measurements of hydrocarbons (Solar Estates), concentrations of 1,3-butadiene, significantly above background levels, were observed under southwesterly winds until late-2009. Around late 2009, major process changes were made at an industrial chemical facility three miles southwest of the Solar Estates site, and concentrations of 1,3-butadiene returned to background levels. Because winds from the southwest are infrequent, the exact date of the change is difficult to determine.

- Sulfur dioxide concentrations decreased significantly since the project began. One site, the J. I. Hailey CAMS 630 site located near the port, measured concentrations that did not comply with the U.S. Environmental Protection Agency (EPA) 2010 National Ambient Air Quality Standards (NAAQS) for sulfur dioxide until 2013. Emissions from ships at docks were shown to have been a likely source of the SO_2, affecting the CAMS 630 site and several other monitoring sites. During the project, environmental regulations were implemented that required reduced sulfur content in ship fuel. After the implementation of the regulations, ambient SO_2 concentrations decreased.

- At two of the monitoring sites (Solar Estates and FHR Easement), an unknown SO_2 interferent was detected periodically. The last observed instance of this SO_2 interferent was December 2013. An experiment showed that the interferent affected different SO_2 instruments differently, but the actual interferent chemical was not identified.

- Hydrogen sulfide monitoring showed decreased concentrations over time at some sites but not others. Three project sites and one TCEQ site measured occasional H_2S concentrations exceeding TCEQ 80 ppb rolling 30-minute standard over the course of the project. The last exceedance observed by the network was in 2012.

3.8 Glossary of Terms for Chapter 3

- **Pollutant concentrations** – Concentrations of most gaseous pollutants are expressed in units denoting their "mixing ratio" in air; i.e., the ratio of the number molecules of the pollutant to the total number of molecules per unit volume of air. Because concentrations for all gases other than molecular oxygen, molecular nitrogen, and elemental argon are very low, the mixing ratios are usually scaled to express a concentration in terms of "parts per million" (ppm) or "parts per billion" (ppb). Sometimes the units are explicitly expressed as ppm-volume (pp<u>m</u>V) or ppb-volume (pp<u>b</u>V) where 1 ppmV indicates that one molecule in one million molecules of ambient air is the compound of interest and 1 ppbV indicates that one molecule in one billion molecules of ambient air is the compound of interest. In general, air pollution standards and health effects screening levels are expressed in ppmV or ppbV units. Because hydrocarbon species may have a chemical reactivity related to the number of carbon atoms in the molecule, mixing ratios for these species are often expressed in ppb-carbon (ppbV times the number of carbon atoms in the molecule), to reflect the ratio of carbon atoms in that species to the total number of molecules in the volume. This is relevant to our measurement of auto-GC species and TNMHC, which are reported in ppbC units. For the purpose of relating hydrocarbons to health effects, this report notes hydrocarbon concentrations in converted ppbV units. However, because TNMHC is a composite of all species with different numbers of carbons, it cannot be converted to ppbV. Pollutant concentration measurements are time-stamped based on the start time of the sample, in Central Standard Time (CST), with sample duration noted.

- **Auto-GC** – The automated gas chromatograph collects a sample for 40 minutes, and then automatically analyzes the sample for a target list of 46 hydrocarbon species. These include benzene and 1,3-butadiene, which are air toxics, various species that have relatively low odor thresholds, and a range of gasoline and vehicle exhaust components. Auto-GCs operated at Solar Estates CAMS 633 and Oak Park CAMS 634. In June 2010, TCEQ began operating an auto-GC at Palm CAMS 83 at 1511 Palm Drive in the Hillcrest neighborhood.

- **Total non-methane hydrocarbons (TNMHC)** – TNMHC represent a large fraction of the total volatile organic compounds released into the air by human and natural processes. TNMHC is an unspeciated total of all hydrocarbons, and individual species must be resolved by other means, such as with canisters or auto-GCs. However, the time resolution of the TNMHC instrument is much shorter than the auto-GC, and results are available much faster than with canisters. TNMHC analyzers were initially operated at all sites, but after April 2012 only operated at the sites that did not take continuous hydrocarbon measurements with auto-GCs.

- **Canister** – Electro-polished stainless steel canisters are filled with air samples when an independent sensor detects that *elevated* (see below) levels of hydrocarbons (TNMHC) are present. Samples are taken for 20 minutes to try to capture the chemical make-up of the air. In most cases, the first time on any day that the monitored TNMHC concentration exceeded 2000 ppbC at a site for a continuous period of 15 minutes or more, the system

would trigger and a sample will be collected. Samples were sent to UT Austin and were analyzed in a laboratory to resolve some 60 hydrocarbon and 12 chlorinated species concentrations. Canister samplers were initially operated at all sites, but after February 2009 were operated the sites that did not take continuous hydrocarbon measurements with auto-GCs.

- **Air Monitoring Comparison Values (AMCV) –** The TCEQ uses AMCVs in assessing ambient data. Two valuable online documents ("Fact Sheet" and "Uses of ESLs and AMCVs Document") that explain AMCVs are at http://www.tceq.texas.gov/toxicology/AirToxics.html (accessed July 2016). The following text is an excerpt from the TCEQ "Fact Sheet" document:

> Effects Screening Levels are chemical-specific air concentrations set to protect human health and welfare. Short-term ESLs are based on data concerning acute health effects, the potential for odors to be a nuisance, and effects on vegetation, while long-term ESLs are based on data concerning chronic health and vegetation effects. Health-based ESLs are set below levels where health effects would occur whereas welfare-based ESLs (odor and vegetation) are set based on effect threshold concentrations. The ESLs are screening levels, **not ambient air standards.** Originally, the same long- and short-term ESLs were used for both air permitting and air monitoring.
>
> There are significant differences between performing health effect reviews of air permits using ESLs, and the various forms of ambient air monitoring data. The Toxicology Division is using the term "air monitoring comparison values" (AMCVs) in evaluations of air monitoring data in order to make more meaningful comparisons. "AMCVs" is a collective term and refers to all odor-, vegetative-, and health-based values used in reviewing air monitoring data. Similar to ESLs, AMCVs are chemical-specific air concentrations set to protect human health and welfare. Different terminology is appropriate because air *permitting* and air *monitoring* programs are different.

- **Rationale for Differences between ESLs and AMCVs** – A very specific difference between the permitting program and monitoring program is that permits are applied to one company or facility at a time, whereas monitors may collect data on emissions from several companies or facilities or other source types (e.g., motor vehicles). Thus, the protective ESL for permitting is set lower than the AMCV in anticipation that more than one permitted emission source may contribute to monitored concentrations.

- **National Ambient Air Quality Standards (NAAQS) –** U.S. Environmental Protection Agency (EPA) has established a set of standards for several air pollutions described in the Federal Clean Air Act. NAAQS are defined in terms of *levels* of concentrations and particular *forms*. For example, the NAAQS for particulate matter with size at or less than 2.5 microns ($PM_{2.5}$) has a *level* of 12 micrograms per cubic meter averaged over 24-hours, and a *form* of the annual average based on four quarterly averages, averaged over three years. Individual concentrations measured above the level of the NAAQS are called *exceedances*. The number calculated from a monitoring site's data to compare to the level of the standard is called the site's *design value*, and the highest design value in the area for a year is the regional design value used to assess overall NAAQS compliance. A monitor or a region that does not comply with a NAAQS is said to be *noncompliant*. At

some point after a monitor or region has been in noncompliance, the U.S. EPA may choose to label the region as *nonattainment*. A nonattainment designation triggers requirements under the Federal Clean Air Act for the development of a plan to bring the region back into compliance.

A more detailed description of NAAQS can be found on the EPA's Website at https://www.epa.gov/criteria-air-pollutants/naaqs-table (accessed July 2016).

One species measured by this project and regulated by a NAAQS is sulfur dioxide (SO_2). EPA set the SO_2 NAAQS to include a level of 75 ppb averaged over one hour, with a form of the three-year average of the annual 99th percentiles of the daily maximum one-hour averages. If measurements are taken for a full year at a monitor, then the 99th percentile would be the fourth highest daily one hour maximum. There is also a secondary SO_2 standard of 500 ppb over three hours, not to be exceeded more than once in any one year.

- **Elevated Concentrations** – In the event that measured pollutant concentrations are above a set threshold they are referred to as "elevated concentrations." The values for these thresholds are summarized by pollutant below. As a precursor to reviewing the data, the reader should understand the term "*statistical significance*." In the event that a concentration is higher than one would typically measure over, say, the course of a week, then one might conclude that a specific transient assignable cause may have been a single upwind pollution source, because experience shows the probability of such a measurement occurring under normal operating conditions is small. Such an event may be labeled "statistically significant" at level 0.01, meaning the observed event is rare enough that it is not expected to happen more often than once in 100 trials. This does not necessarily imply the occurrence of a violation of a health-based standard. A discussion of "elevated concentrations" and "statistical significance" by pollutant type follows:

    - For H_2S, any measured concentration greater than the level of the state residential standards, which is 80 ppb over 30 minutes, is considered "elevated." For SO_2, any measured concentration greater than the level of the NAAQS, which is 75 ppb over one hour, is considered "elevated." Note that the concentrations of SO_2 and H_2S need not persist long enough to constitute an exceedance of the standard to be regarded as elevated. In addition, any closely spaced values that are statistically significantly (at 0.01 level) greater than the long-run average concentration for a period of one hour or more will be considered "elevated" because of their unusual appearance, as opposed to possible health consequence. The rationale for doing so is that unusually high concentrations at a monitor may suggest the existence of unmonitored concentrations closer to the source area that are potentially above the state's standards.
    - For TNMHC, any measured concentration greater than the canister triggering threshold of 2000 ppbC is considered "elevated." Note that the concentrations need not persist long enough to trigger a canister (900 seconds) to be considered elevated.

- For benzene and other air toxics in canister samples or auto-GC measurements, any concentration above the AMCV is considered "elevated." Note that 20-minute canister samples and 40-minute auto-GC measurements are both compared with the short-term AMCV.
- Some hydrocarbon species measured in canister samples or by the auto-GC generally appear in the air in very low concentrations close to the method detection level. Similar to the case above with H_2S and SO_2, any values that are statistically significantly (at 0.01 level) greater than the long-run average concentration at a given time or annual quarter will be considered "elevated" because of their unusual appearance, as opposed to possible health consequence. The rationale for doing so is that unusually high concentrations at a monitor may suggest an unusual emission event in the area upwind of the monitoring site.